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The Dissociation of H_2O into H+OH*

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The energy of dissociation of H_2O into H+OH was measured by an experiment developed from the method of Bonhoeffer and Reichardt. A spectrograph of high resolving power served for the measurement of the intensity of the absorption spectrum of OH in a heated mixture of water vapor and oxygen. The result (for 0°K) was $H+OH \rightarrow H_2O - 118.2 \pm 0.7$ kcal. and $O+H \rightarrow OH - 100.1 \pm 0.9$ kcal. The probabilities of transition of the lines of the OH band were recomputed.

I. PROBLEM

THE energy of dissociation of H_2O molecules *into atoms* H+H+O is known accurately. It is derived from the thermal measurement of the explosion $2H_2+O_2 \rightarrow 2H_2O$ and the spectroscopic investigation of the molecules H_2 and O_2. The energy of dissociation of H_2O *into H atoms and OH radicals*, or, closely connected with it, the energy of dissociation of free OH radicals, is much less accurately known. The importance of this latter dissociation process was first pointed out by Bonhoeffer and Reichardt.[1] They furnished the first determination of its energy by a method which basically still seems most reliable although it is subject to certain sources of error. Because of such errors, Gordon,[2] in his comprehensive treatment of dissociation energies, came to the conclusion that "unfortunately a reliable calculation of the hydroxyl dissociation is not possible at present because of the uncertainty as to the energy of dissociation."

In the measurement of Bonhoeffer and Reichardt there is a systematic error due to the lack of resolving power of the spectrograph. The absorption spectrum of free OH consists of rotational lines at irregular mutual distances, most of them widely separated from each other compared with the line width because of the small moment of inertia of OH (Fig. 1).[3] Consequently a spectrograph of small resolving power, as used by Bonhoeffer and Reichardt, which fails to resolve single lines but shows the whole band as a short, nearly continuous spectrum (see reproduction in reference 1), requires a relatively high concentration of OH. For a quantitative test by the absorption spectrum rather weak absorption is desired. But at this high concentration, although the *average* absorption observed with a spectrograph of poor resolving power may be weak, the *actual* absorption contains many lines each one of them at its middle almost completely absorbing the incident radiation; in this case the concentration of OH affects the total intensity transmitted only by the more or less extended wings of the lines. Therefore, the broadening of the lines is essential for the over-all absorption observed. In the method under discussion pairs of

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[1] K. F. Bonhoeffer and H. Reichardt, Zeits. f. physik. Chemie **A139**, 75 (1928).

[2] A. R. Gordon, J. Chem. Phys. **1**, 308 (1933). The results of the various methods were recently surveyed by G. Damköhler and R. Edse, Naturwiss. **31**, 310 (1943).

[3] See O. Oldenberg, J. Chem. Phys. **3**, 270 (1935). The effect of the resolving power is discussed in J. Chem. Phys. **7**, 487 (1939).

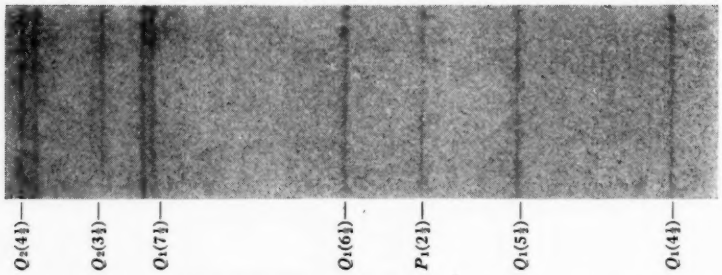

FIG. 1. Part of OH band 3064A (absorption, positive, 10 times enlarged). For the reproduction a spectrum is selected with more intense absorption lines than for the measurement.

absorption spectra are matched. The two members of such a pair, however, are subject to pressure broadening by widely different mixtures of O_2+H_2O (66.7 percent and 0.59 percent of H_2O, respectively) which may have different broadening effects. All that is known are the broadening effects on the mercury line 2537;[4] here H_2O has an effect stronger than O_2 by the factor 1.35. Therefore, two absorption spectra, taken at high concentration without resolving the lines, do not reliably indicate equal concentrations of OH by their equal intensities. Figure 1 shows that the single absorption lines are very narrow as compared with their mutual distances; this spectrum makes it evident that, for an accurate comparison of intensities, *single lines* should be observed rather than the *apparent continuum* produced by their broadening and lack of resolving power. It is not possible, however, to estimate the systematic error that may be caused by such a broadening. The ideal instrument would have a resolving power large as compared with the line width and so reveal the contours of the absorption lines.

As at this laboratory the absorption spectrum of free hydroxyl has been investigated with high resolving power for another purpose—the study of the kinetics of free hydroxyl—it seemed desirable to apply this technique to a more accurate measurement of the energy of dissociation of H_2O into H+OH, based on the work of Bonhoeffer and Reichardt. As will be shown in the survey of the different methods given in the following section, this method when carried out with a spectrograph of high resolving power gives the best prospect of high accuracy. This measurement is the subject of the present paper. The higher accuracy which is aimed at necessitates some other changes, in particular in the measurement of the temperature. A further improvement is due to the development of spectroscopic thermodynamics, which has taken place within the last decade. Spectroscopy furnishes reliable data for the computation of the specific heats and the chemical constants of all molecules involved.

Apart from the chemical interest, this energy of dissociation enters into the measurement of the "*f* values" of OH radicals;[5] furthermore, it is of interest for the study of the solar atmosphere where Russell[6] found a discrepancy between the values of the abundance of OH estimated by different methods. This aspect will be discussed somewhere else.

II. PREVIOUS WORK

The work of Bonhoeffer and Reichardt,[1] which will be discussed in detail in Section III, gave the energy of dissociation of $H_2O \rightarrow H+OH$ as 115 kcal. with an estimated probable error of 2.5 kcal.; but this limit included only the *accidental* error, estimated by the conventional method, and did not take into account the *systematic* error pointed out in the preceding section.

Avramenko and Kondratjew[7] modified the method of Bonhoeffer and Reichardt by resolving the single lines of the OH band with a large Hilger quartz spectrograph. As a background they used the line spectrum from an electric discharge tube. They were forced to make rather arbitrary assumptions regarding the widths of their lines. Furthermore, they presupposed "weak absorption," although it may be difficult to decide whether weak absorption *observed with their inadequate resolving* power really indicates weak absorption *in the middle of the line*. Their

[4] C. Fuechtbauer, G. Joos, and O. Dinkelacker, Ann. d. Physik **71**, 220 (1923).

[5] O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 439 (1938).

[6] H. N. Russell, Astrophys. J. **79**, 325 (1934), Table III.

[7] L. Avramenko and V. Kondratjew, Acta Physicochimica **8**, 567 (1937). See O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 169 and 779 (1938).

accuracy was further impaired by a small temperature range (1200–1320°C). Their result for the energy, $H_2O \rightarrow H+OH-113.5$ kcal., was given without an estimate of the error, as this measurement was only incidental in an investigation largely concerned with other problems.

A different spectroscopic method was applied by Senftleben and his collaborators,[8] and by Wood and Gaviola.[9] In the most recent work of this group, Riechemeier, Senftleben, and Pastorff illuminated water vapor, to which a trace of mercury vapor was added, with the resonance line of mercury and so produced gaseous hydrogen. In accord with the work of Cario and Franck,[10] they assumed that the excited mercury atoms transferred their energy of 4.86 ev to the water molecules and so caused their dissociation into H+OH. This process requires slightly more energy than is available as excitation energy of the mercury atoms. Therefore, it can occur only at collisions with excess thermal energy. The authors measured the yield of H_2 as a function of the temperature and compared their results with the theoretical expression based on the Boltzmann formula. Thus for the energy of $H_2O \rightarrow H+OH$ they obtained 5.07 ± 0.04 ev or 117.0 ± 0.9 kcal. (For the excitation energy of Hg atoms, the authors applied 4.9 instead of 4.86 ev. For this reason we corrected their final result by -0.04 ev. $= -1$ kcal. However, their method is such that an additive correction is not strictly correct.)

Two objections to this argument may be raised. First, it is not certain whether the hydrogen is formed by the dissociation process just mentioned or, instead, by the intermediate formation of HgH molecules in the process $Hg' + H_2O \rightarrow HgH + OH$ followed by a reaction in which the rather unstable HgH molecules give off their H atoms. (The analogous formation of HgH is well established in the collisions of excited mercury atoms with hydrogen molecules.) This intermediate process would require less energy by the energy of formation of HgH ($=0.369$ ev). If such molecules are formed, the numerical result given above would be too low.

The other objection is more fundamental in that it applies to all methods in which a *non-equilibrium* is observed. In this method it is presupposed that for any thermal collision taking place above the energy of dissociation the intrinsic probability of the reaction is the same. On this basis the temperature effect on the rate of the reaction is determined only by the Boltzmann factor. It is disregarded that the intrinsic probability of collisions of the second kind may gradually vary with the excess energy of the collisions. Conventionally such a variation is described by the "excitation function." This function is unknown. It should not affect the result of the equilibrium method; but if, for example, the intrinsic probability is *increasing* with increasing energy, the non-equilibrium method would yield *too large* a value for the limiting energy. It is true that, for the non-equilibrium method under discussion, the excitation function needs to be considered only for the narrow energy range of thermal motion. On the other hand, at least for *atomic* energy levels, the excitation functions are known to vary rapidly within a narrow range right above the limit.[11]

Finally, the energy of dissociation $H_2O \rightarrow H+OH$ has been determined by the explosion method.[12] The most recent and accurate experiment was performed by Lewis and von Elbe. This method is subject to many corrections.[13] Lewis and von Elbe derived the energy 114000 ± 1000 kcal. for the same dissociation process.

The survey of various methods given here seems to indicate that the method of Bonhoeffer and Reichardt, when applied with a spectrograph of high resolving power, offers the best prospect for high accuracy.

III. THE EQUILIBRIUM $4OH \rightleftarrows 2H_2O + O_2$

Following Bonhoeffer and Reichardt, we consider the thermal dissociation of H_2O vapor with excess O_2 added:[14]

$$4OH = 2H_2O + O_2 + \Delta H_T. \qquad (1)$$

[8] O. Riechemeier, H. Senftleben, and H. Pastorff, Ann. d. Physik **19**, 202 (1934).
[9] R. W. Wood and E. Gaviola, Phil. Mag. **6**, 1191 (1928).
[10] G. Cario and J. Franck, Zeits. f. Physik **11**, 161 (1922).
[11] W. Hanle, Zeits. f. Physik **54**, 848 (1929); **56**, 94 (1929); **65**, 512 (1930).
[12] K. Wohl and M. Magat, Zeits. f. physik. Chemie **B19**, 117 (1932); B. Lewis and G. von Elbe, J. Chem. Phys. **3**, 63 (1935).
[13] See A. Eucken, "Energie und Waermeinhalt," *Handbuch der Experimental-Physik* **8**, Part 1, 369 (1929); K. Wohl and G. von Elbe, Zeits. f. physik. Chemie **B5**, 241 (1929).
[14] We follow the notation of S. Glasstone, *Textbook of Physical Chemistry* (D. Van Nostrand Company, Inc., New York, 1940).

From this energy ΔH_T, reduced to zero degrees, and certain other known energies, we shall derive the energy ΔU_0^0 of the reaction we are interested in,

$$H+OH=H_2O+\Delta U_0^0. \quad (2)$$

A. Theory

1. The Measurement of ΔH_T

As the underlying theory presented here largely follows the argument given by Bonhoeffer and Reichardt,[1] we shall omit the detail of the computations.

When we write the partial pressures of H_2O, O_2, and OH as x, y, and z, respectively, the equilibrium constant of reaction (1) is

$$K=x^2y/z^4. \quad (3)$$

While we can vary x and y at will, we want to determine z by the intensity of the absorption spectrum of OH. The experiments are carried out at constant pressure ($P=775$ mm). We restrict ourselves to temperatures so low that the hydroxyl pressure z is very small as compared with x and y. We can vary at will the ratio of x to y at constant T and P; thus the partial pressure z of OH varies and reaches a maximum for $x=\frac{2}{3}P$ and $y=\frac{1}{3}P$, that is, for equal numbers of bound H atoms and O atoms. This is called the "optimum mixture."

ΔH_T is derived from the Van't Hoff isochore, which, when integrated between the temperatures T_1 and T_2, with the application of Eq. (3), leads to Eq. (4):

$$\Delta H_T=[4RT_1T_2\ln(z_2/z_1)]/(T_1-T_2). \quad (4)$$

In this integration we assume that ΔH_T does not vary between T_1 and T_2; this will be checked later. (Subscript 1 indicates the higher and 2 the lower temperature.)

The most satisfactory application of absorption spectra consists of matching two absorption lines of *equal intensity* and so testing the two absorbing mixtures for *equal density* of the absorbing molecules. In order to apply this method to two gas mixtures at different temperatures Bonhoeffer and Reichardt[1] reduced the partial pressure of OH at the higher temperature T_1 by adding more oxygen and so changing the mixture from its optimum composition, at constant total pressure P. Thus they reduced the OH partial pressure to such a value z_1' that, in spite of the high temperature T_1, the absorption spectrum was only as intense as that of the optimum mixture at the low temperature. The ratio z_1'/z_1 follows from the mass action law:

$$z_1'/z_1=\{[27x_1'^2(P-x_1')]/4P^3\}^{\frac{1}{4}}. \quad (5)$$

The partial pressure x_1' of the water vapor is at our disposal, the total pressure P being constant. (The prime indicates the equilibrium shifted by the excess of oxygen, while letters without a prime indicate optimum mixtures; hence $x_1=2P/3$.)

By matching absorption lines we identify a pair of mixtures with equal *density* of OH. Hence this experiment, in which two mixtures are compared at different temperatures, gives the following evidence regarding *partial pressures:*

$$z_1'/z_2=T_1/T_2. \quad (6)$$

In order to apply Eq. (4) we wish to know z_2/z_1. This follows by dividing the last two equations. Introducing the result into (4) we obtain:

$$\Delta H_T=\frac{4RT_1T_2\ln\left(\frac{z_1'}{z_1}\times\frac{T_2}{T_1}\right)}{T_1-T_2}. \quad (7)$$

This theory leads to the following procedure: Select the total pressure P a little higher than one atmosphere so that inside the chamber there is always a slight excess pressure. Select T_2 as the minimum temperature at which, with the optimum mixture, the absorption spectrum of OH is still observable. Select an arbitrary value of x_1' considerably smaller than the optimum value of $\frac{2}{3}P$. Next determine the corresponding temperature T_1, defined as the temperature of equal intensities of absorption lines; experimentally this temperature is found by taking absorption spectra at various temperatures. For the highest accuracy, a value of x_1' must be determined by trial and error so that the temperature T_1 is as high as can be reached with the oven. (Our present knowledge of ΔH_T may serve for predicting a reasonably good value of x_1', once T_1 is given as the highest temperature to be reached.) These are the temperatures and pressures which must be introduced into the above equation (7).

2. Corrections

Errors may be caused by (a) the non-uniform temperature distribution, (b) the difference in the Boltzmann distributions between the two temperatures, and, finally, (c) the variation of ΔH_T over the temperature range T_1-T_2.

(a). Introducing $z_2/z_1=(z_1'/z_1)(T_2/T_1)$ into Eq. (5) involves an error in that a uniform temperature over the length of the oven is presupposed. For non-uniform temperature equal absorption lines indicate that the integrals of the densities of OH, taken over the length of the tube, are the same for both absorbing mixtures. For this case Bonhoeffer and Reichardt, who used a graphite tube resistance furnace along which the temperature could not be equalized, applied a method of successive approximations.

The first application of their method to our experiment resulted in a very small correction for ΔH_T, less than 0.3 percent. The constancy of the temperature along the oven was responsible for this favorable result. Another procedure to simplify the labor required in the calculation of the other plates immediately suggested itself. As the correction was so small, much smaller than the probable error estimated below, and as all plates were taken at nearly the same two temperatures, it may be assumed that the same correction applies to all plates. Consequently, Eq. (7) may be written in the corrected form

$$\Delta H_T=\frac{4RT_1T_2\cdot\ln\left(\frac{Cz_1'}{z_1}\right)\left(\frac{T_2}{T_1}\right)}{T_1-T_2}.$$

The correction factor C; taken from the first plate, was 0.993.

(b). In the theoretical discussion (Section III, A1) we assumed that *equal intensities of absorption lines indicate equal densities of the absorbing gas.* As we were observing single absorption lines, unlike Bonhoeffer and Reichardt, this statement applied to the density not of OH, but only of the rotational level responsible for the absorption line under observation. From the energy levels (electronic, vibrational, and rotational) the populations of the various rotational levels (zero vibration, electronic level $^2\Pi_{1/2}$) which absorb the Q_1 branch were computed for $T_1=1360°K$ and $T_2=1176°K$. As stated in a preceding paper,[3] the line $Q_1(6\frac{1}{2})$ served best, because it is near the intensity maximum and has only a weak satellite.

As will be described below, the matching was not so accurate that for one pair matched other pairs could be observed as non-matched, that is, the difference between the thermal distributions at 1176°K and 1360°K could not be noticed. As the procedure involves no preference for one or the other spectrum, no *systematic* error is to be expected. The spread of results (Table I) is due to *accidental* errors in the matching of absorption lines.

(c). At the integration of the Van't Hoff isochore we put ΔH_T in front of the integral and so assumed its constancy between T_1 and T_2. The change in ΔH as a function of temperature is expressed by Kirchhoff's formula,

$$\Delta H_{T_2}-\Delta H_{T_1}=\int_{T_1}^{T_2}\Delta C_p dt.$$

The value of ΔC_p for the reaction of Eq. (1) is

$$\Delta C_p=2C_{H_2O}+C_{O_2}-4C_{OH}.$$

These specific heats (all taken at constant pressure) have been calculated from spectroscopic data and published for O_2 by Johnston and Walker,[15] for OH by Johnston and Dawson,[16] and for H_2O by Gordon.[17] Gordon's calculations assumed a rigid molecule, so the correction formula for rotational distortion given by Wilson[18] was applied; using the correction term obtained by Stephenson and McMahon.[19] In this manner it was calculated that the value of ΔH changed only 130 calories per mole between 900°C and 1100°C, the range of temperatures used in the experiment. As this is less than 0.1 percent of the total value, the assumption of constant ΔH in the integration was clearly justified.

3. Reduction to Standard Pressure and Temperature

While we measured the energy ΔH_T *at 775 mm pressure*, we want to determine the energy ΔH_T^0

[15] H. L. Johnston and M. K. Walker, J. Am. Chem. Soc. **55**, 172 (1933).
[16] H. L. Johnston and D. H. Dawson, J. Am. Chem. Soc. **55**, 2744 (1933).
[17] A. R. Gordon, J. Chem. Phys. **2**, 64 and 549 (1934).
[18] E. B. Wilson, J. Chem. Phys. **4**, 528 (1936).
[19] C. C. Stephenson and H. O. McMahon, J. Chem. Phys. **7**, 614 (1939).

at the standard pressure of 760 mm. Both energies are equal.[20]

Finally, the reduction to zero temperature is to be carried out with the formulas and tables of spectroscopic thermodynamics as follows. The entropy S and the free energy function $-(G^0-U_0^0)/T$ have been tabulated[21] as functions of the temperature for all molecules involved. Surveys of this field have recently been given by Wilson and by Zeise.[22]

The entropies and free energies were obtained from the tables of Johnston and Dawson[16] on OH, Johnston and Walker[15] on O_2, and Gordon[17] on H_2O. As in the case of specific heats, Gordon's values were corrected for rotational distortion by Wilson's[18] formula using the correction constant of Stephenson and McMahon.[19]

The heat of reaction at absolute zero ΔU_0^0 is[23]

$$\Delta U_0^0=\Delta H_T^0-T\Delta S_T^0+T\Delta\left(-\frac{G_T^0-U_0^0}{T}\right). \quad (8)$$

In this equation ΔH_T^0 is taken from our measurements and the other quantities from tables.

[20] See S. Glasstone, reference 14, p. 230, Eq. (149), applied to the ideal gas law.

[21] The formulas are given by S. Glasstone, reference 14, for the entropy S on p. 865, Eq. (179); for the free energy function $(G^0-U_0^0)/T$ on p. 865, Eq. (180).

[22] E. B. Wilson, Chem. Rev. **27**, 17 (1940). H. Zeise, Zeits. f. Electrochemie **43**, 704 (1937); **48**, 425, 476, and 693 (1942).

[23] S. Glasstone, reference 14, p. 866, Eq. (182).

B. Experimental Procedure

1. The Oven and the Measurement of the Temperature

The oven (Fig. 2) consisted of a ceramic tube (length 5 feet, o.d. 6 cm), wound with Nichrome V ribbon, thermally insulated to about 3″ from the ends. In order to equalize the temperature over as long a section as possible, the heater winding was provided with nine taps, in addition to the free ends. The end sections from which the dissipation of heat was greatest carried the full current; toward the middle of the oven the current was adjusted to smaller values by shunts. With this arrangement it was possible to equalize the temperature to within 2°C over a central portion 85 cm in length. It then dropped off rapidly toward the ends.

The oven was provided with a thermostat which was built by Dr. H. S. Sommers, Jr., following the design given by Bancroft.[24] A thin platinum wire, embedded in the oven, formed one branch of a Wheatstone bridge. By its change of resistance it operated a thyratron which, in turn, regulated the heating current. This regulator is capable of holding the temperature of the oven constant to a fraction of a degree.

The temperature distribution along the oven was measured by a platinum, platinum-rhodium

[24] D. Bancroft, Rev. Sci. Inst. **13**, 24 and 114 (1942).

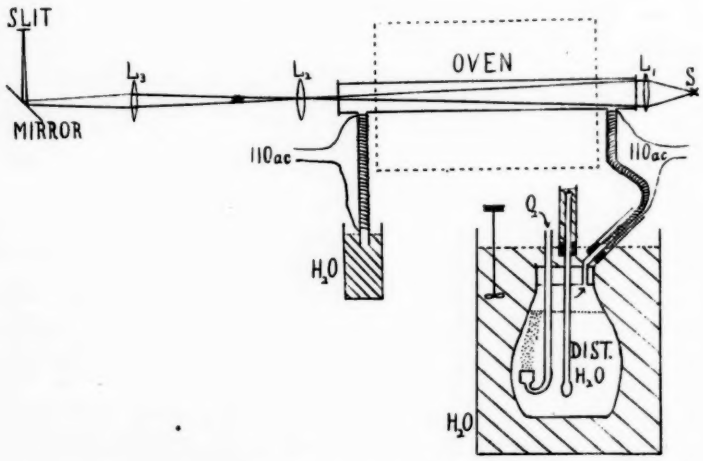

FIG. 2. Experimental arrangement for the measurement of the absorption spectrum of heated water vapor.

thermocouple. Within the oven the thermocouple was protected by a long, narrow quartz tube.

Considerable trouble was experienced because of the deterioration of the quartz tube in the heated mixture of H_2O and O_2. After some weeks of heating the quartz turned brittle. As soon as a leak developed, the thermocouple was exposed to the vapors and so deteriorated. For the final measurements a new quartz tube was used, also a new thermocouple which was exposed to the high temperature for as short periods as possible; its wires were insulated from each other by a thin quartz tube since the Alundum tube used in the first experiments seemed to affect the wire. Moreover, insulating by means of a thin quartz tube is advantageous because of its small thermal inertia.

One end of this tube inside the oven was closed and so prevented direct contact of the thermocouple with the water vapor; the other end was sealed through one of the quartz windows and was open so that the thermocouple could slide in and out. The thermoelectric force was measured by a potentiometer against a standard cell which, in turn, was calibrated against another cell recently checked by the Bureau of Standards.

The thermocouple wires were checked for homogeneity[25] at intervals during the progress of the experiment. At no time did they develop electromotive forces sufficient to cause errors of over half a degree at the highest temperatures used. The thermocouple was calibrated against the melting point of pure gold.

For the accuracy of the method, the ease with which the temperature can be adjusted and measured is of importance. Here again the high resolving power of the grating is responsible for a marked improvement in the method. The reason is that it brings down the highest temperature applied from 1590° to 1100°C. Here the temperature of the oven can more easily be measured and kept constant over its length.

2. *The Mixtures of Water Vapor and Oxygen*

In order to be independent of the daily variations of the atmospheric pressure, we maintained a constant pressure of $P=775$ mm, slightly above the ordinary pressure. This pressure was easily kept constant by adjusting the height of the water level (Fig. 2) through which the mixture bubbled at the outlet side of the large tube. With this arrangement, minor leaks could not disturb the content of the tube, any leakage being from inside to outside.

The *optimum mixture* of H_2O and O_2 was produced by the apparatus shown in Fig. 2. The water vapor pressure had to be $\frac{2}{3}P=516\frac{2}{3}$ mm. This was produced by bubbling oxygen in very small bubbles through distilled water of 89.53°C. The temperature of the distilled water was kept constant by a water bath, permanently stirred, the temperature of which was controlled through a mercury thermostat. The temperature of the distilled water was measured by a mercury thermometer calibrated against a standard thermometer which, in turn, was calibrated by the Bureau of Standards. It was possible to estimate to 0.01°C. (In order to apply the proper correction, the temperature of the stem was kept constant by a coaxial tube containing water, a stirrer, and another small thermometer.) The principal difficulty in maintaining the temperature of the distilled water constant was in maintaining the rate of flow of the oxygen constant, a precaution necessary because of the cooling by evaporation. Therefore a standard rate of flow was maintained by observing the rate of bubbling at the exit jar. Experiment showed that this was proportional to the rate of flow. The rate corresponded to a velocity of approximately 0.23 cm/sec. through the tube, or 16 liters/hour for the mixture. The temperature of the distilled water was constant within 0.04°. In order to prevent condensation of the water vapor, every part of the system was maintained at a temperature higher than that of the bath in which the mixture was formed.

The flowing mixture had a measurable effect on the end of the oven it entered first, so the shunting resistors were adjusted to equalize this temperature while the mixture was flowing at the standard rate. In order to check the apparatus, the resulting mixture was analyzed and found satisfactory.

The *non-optimum mixture* should deviate strongly from the optimum mixture which had a water vapor pressure of $516\frac{2}{3}$ mm. We chose the water vapor pressure at 0°C, that is $x_1'=4.58$ mm. As found by trial and error, this mixture needed a temperature well within the reach of a

[25] W. F. Roeser and H. T. Wensel, National Bureau of Standards, Research Paper RP768 (March, 1935).

Nichrome wound oven (around 1100°C) in order to produce the same intensity of absorption lines as the optimum mixture at 900°C. This partial pressure of water vapor was produced by bubbling oxygen of slightly more than 1 atmos. through two successive deep vessels containing water of 0°C, the temperature of which was kept constant with an ice bath.

This choice of x_1' leads to the ratio of the two OH partial pressures, non-optimum and optimum, z_1'/z_1 by Eq. (5).

$$\log (z_1'/z_1) = -0.9066.$$

3. *The Optical Arrangement*

The OH absorption band at 3064A was observed in the second order of a 21-foot concave grating. In order to increase the intensity, the grating was covered with a thin coating of aluminum evaporated in vacuum.[26] The grating at our disposal, ruled by Rowland, had nearly the theoretical resolving power, which was not impaired by the aluminum plating. At the spectral range near 3000A this resolving power was 0.015A. It permitted a wide separation of the single lines of the absorption band (Fig. 1). It almost permitted a resolution of the contour of each single absorption line, its width being 0.054A. These figures show that the apparatus nearly reached the ideal case of a resolving power high as compared with the width of the absorption line.

A hydrogen discharge tube, constructed by N. D. Smith,[27] furnished the continuous background. Eastman Spectroscopic Plates III-O were used as the best compromise between resolution and exposure time, which was 30 min.

First one exposure of the OH absorption spectrum was taken with the optimum mixture and the temperature near 900°C, then a series of six or seven was taken with the non-optimum mixture causing the oven temperature to vary in steps of five to ten degrees. After the development the plate was split, the 900° exposure being separated from the series taken around 1100°. The object then was to match one of this series with the exposure at 900°C.

We agree with Bonhoeffer and Reichardt in that the eye is well able to match absorption spectra, so that the densitometer does not improve the results. For the visual matching of absorption lines rather low intensities of absorption turned out to be useful. The order of magnitude was 8 percent absorption at the middle of the lines. For such lines densitometer traces are less satisfactory because the grain is prominent. Two plates were matched by placing them so that the lines on one plate appeared to run into the same lines on the other plate. Where the backgrounds of the two plates were equal, it was convenient to match the lines under a binocular microscope possessing a broad field of view which permitted the entire spectrum on the plates to be seen as a whole. Where the backgrounds were slightly different, it was better to match the lines with a special comparator,[28] with which background variations could be compensated. In general, if one line on one plate was stronger than the same line on the other plate, one could observe that all lines on the one were stronger than the same lines on the other. This indicated that the variation with rotational distribution between the temperatures of 900° and 1100°C was not noticeable; so no correction for this was made.

C. Results

The lowest temperature at which the absorption spectrum of free OH showed up clearly was 768°C. Incidentally, this figure indicates how much more sensitive the test for free OH is with the large grating spectrograph than with the medium-size quartz spectrograph used by Bonhoeffer and Reichardt,[1] who report barely observable absorption at 1150°C. Computed for absorption tubes of equal length, the sensitivity is increased by the factor 45.

The main experimental problem consisted of finding the high temperature T_1 at which the non-optimum mixture (water vapor pressure $x_1' = 4.58$ mm) produced as intense absorption lines as the optimum mixture ($x_2 = 516.7$ mm) at the low temperature T_2. Because of the even temperature distribution along the oven, it was possible to let

[26] We appreciate the help and advice of Mr. John Gilroy who allowed us to use his vacuum evaporation apparatus.
[27] N. D. Smith, J. Opt. Soc. Am. **28**, 40 (1938).

[28] A. A. Frost, D. W. Mann, and O. Oldenberg, J. Opt. Soc. Am. **27**, 147 (1937).

T_1 and T_2 represent the average value of the temperature over a length of 88 cm in the middle portion (see Section III, A2).

Table I gives the results of eight plates. Some other plates had to be discarded because the intensities of either the background or the absorption spectrum turned out to be unfavorable for the photometric comparison.

The formula for the "probable error of the mean" applied to Table I leads to a value of less than 1 kcal. Considering the difficulty of the photometric work, we prefer to give ±2.6 kcal. as what seems to us a liberal estimate of this probable error. This leads to the result for an average temperature of 1250°K:

$$\Delta H_T = 157.5 \pm 2.6 \text{ kcal.}$$

As discussed above (Section III, A2), ΔH_T is practically constant over the whole range of temperatures applied. Hence the reduction to zero temperature by Eq. (8) can be applied to this average value. The result for $T=0$°K is $\Delta U_0^0 = -153.4$ kcal. or

$$4OH = 2H_2O + O_2 - 153.4 \pm 2.6 \text{ kcal.}$$

TABLE I. Survey of results.

Plate No.	T_1 (deg. K)	T_2 (deg. K)	$-\Delta H_T$ (kcal.)	Weight
1	1379	1194	158	½
2	1371	1188	158	½
3	1361	1178	156	1
4	1340	1166	159	1
5	1346	1166	155	1
6	1319	1145	154	½
7	1339	1160	154	1
8	1366	1191	165	1
			average 157.5	

The only source of a *systematic* error which we know of is the lack of resolving power of the spectrograph, as even the large grating at our disposal does not permit a reliable measurement of the complete contours of the absorption lines. In a previous investigation[5] it was found that the widths of these lines are due only one-third to Doppler effect, the other two-thirds representing pressure broadening. Here the lines are observed at a pressure of nearly one atmosphere, this pressure being composed in one experiment of $\frac{2}{3}H_2O+\frac{1}{3}O_2$, and in the other experiment, of $0.006H_2O+0.994O_2$. This gives a chance for comparison of the broadening effects of the molecules H_2O and O_2 on the absorption lines of OH. A difference in the widths of the absorption lines is barely noticeable, H_2O causing a broadening just slightly stronger than O_2.[29] The difference is so small that at first it was overlooked. It can hardly affect the comparison to a considerable extent.

IV. THE EQUILIBRIUM $H_2+2OH \rightleftarrows 2H_2O$

A. The Energy $H+OH \rightarrow H_2O$

As an intermediate step, we compute the energy of $H_2+2OH \rightarrow 2H_2O(g)$ which will be needed in the following section. To the result of the experiments reported, we add the equation for the combustion of molecular hydrogen[30] forming water vapor, which is known from thermochemistry with higher accuracy. The result is

$$H_2+2OH = 2H_2O(g) - 133.8 \pm 1.3 \text{ kcal.}$$

Beutler[31] calculated the energy of dissociation of hydrogen molecules (normal mixture of ortho and para) from spectroscopic data as 102.48 ±0.03 kcal. This leads to the energy of dissociation we are mainly interested in,

$$H+OH = H_2O(g) - 118.2 \pm 0.7 \text{ kcal.}$$

This result agrees, within the limit of error, with the less accurate result of Bonhoeffer and Reichardt,[1] which (applying the more recent value of the energy of dissociation of H_2) is 115.3±2.5 kcal. Furthermore, the result agrees with the result of Senftleben and collaborators[8] (5.07±0.04 ev=117.0±0.9 kcal.). However, as discussed in Section II, we hesitate to consider this agreement as a confirmation, since their non-equilibrium method is subject to two sources of systematic errors. We are not sure whether the accuracies warrant more detailed conclusions regarding the possible processes involved.

Our value is larger than the upper limit which Damköhler and Edse[2] derived from the work of

[29] The mercury line 2537 is broadened by H_2O more strongly than by O_2; see reference 4.

[30] A. R. Gordon, J. Chem. Phys. **1**, 310 (1933). This value is not appreciably affected by Wilson's correction for the stretching of the rotating molecule. The probable error is negligible as compared with the error of our measurements.

[31] H. Beutler, Zeits. f. physik. Chemie **B29**, 315 (1935).

Sharma.[32] We do not believe, however, that it is safe to derive quantitative conclusions from Sharma's experiment. In the ultraviolet absorption spectrum of H_2O_2 he observed a continuous band with an abrupt high frequency limit at 2055A. He attributed this limit to the dissociation process $H_2O_2+h\nu\rightarrow H+H+O_2$ and computed the energy required for this dissociation from the wave-length. This interpretation may be questioned. From the investigation of diatomic molecules it is known that a dissociation process becomes evident, not by a sharp limit of the absorption spectrum, but rather by a transition from a discrete to a continuous spectrum. The reason is that the probabilities of transition (explained by the Franck-Condon principle) do not abruptly vary when, by increasing frequency of light, the final state of the absorption process changes from high vibration to dissociation.[33] It seems hardly possible to invent potential curves for the normal and excited states such that dissociation is connected with a sharp *high frequency* limit of a *continuous* spectrum.

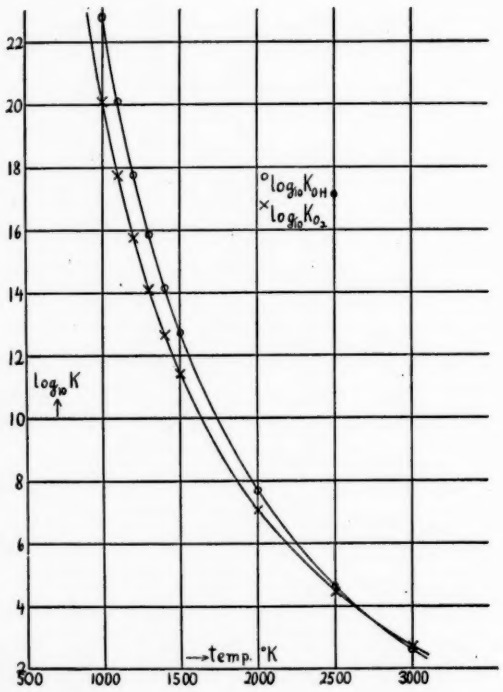

FIG. 3. The equilibrium constants K_{OH} and K_{O_2} as functions of the temperature.

The energy of formation of H_2O from the atoms is 218.3±0.2 kcal. Together with the last equation this leads to the energy

$$O+H=OH-100.1\pm0.9 \text{ kcal.}$$

These energy values apply for 0°K. For higher temperatures, the energies can be computed with the help of the tables referred to in Sections III and IV.

B. The Equilibrium Constant

We are interested in the thermal dissociation of H_2O, without the addition of O_2 which, in the experiments reported, was added for technical reasons. The equilibrium in water vapor is given by

$$H_2+2OH=2H_2O(g)-133.8(\pm1.3) \text{ kcal.}$$

The equilibrium constant K_p which applies to this equilibrium is

$$K_{OH}=[H_2O]^2/[H_2]\times[OH]^2.$$

Its numerical value is derived from the equation (see Section III, A3):

$$\log_{10}K_{OH}=T\Delta\left(-\frac{G^0-U_0^0}{T}\right)\cdot\frac{0.434}{RT}-\Delta U_0^0\frac{0.434}{RT}.$$

Tables for the free energy functions $-(G^0-U_0^0)/T$ have been computed for all molecules involved on the basis of data derived from molecular spectra.[34] The resulting values of K_{OH}, extended up to 3000°K, are given in Table II and Fig. 3.[35]

The accuracy of $\log_{10}K_{OH}$ depends upon the accuracy with which the energy ΔU_0^0, determined in the present paper, and the free energy function $-(G^0-U_0^0)/T$ are known. The papers referred to above give estimates of the accuracy of the free energy functions.

[32] R. S. Sharma, Proc. Ind. Acad. Sci. **4**, 51 (1934).

[33] See G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 409.

[34] The thermodynamic functions for H_2 were obtained from Giauque's table [J. Am. Chem. Soc. **52**, 4821 (1930)] of the free energy function and Davis and Johnston's table [J. Am. Chem. Soc. **56**, 1045 (1934)] of entropies. All the tables used in the present calculation excluded the nuclear contribution except Giauque's table for the free energy function; so in order to use it with the others his values were all reduced by 2.775, the amount he gives as the nuclear contribution.

[35] Zeise computed values of K_{OH} [Zeits. f. Electrochemie **48**, 23 (1942)] on the basis of our preliminary publication of the energy of dissociation [Phys. Rev. **59**, 928 (1941)].

These values of K_{OH} are larger than the ones derived by Bonhoeffer and Reichardt, indicating less hydroxyl dissociation. The values are only slightly beyond the limit estimated by these authors. In order to compare the "*hydroxyl dissociation*" with the well-known "*oxygen dissociation*" of water vapor

$$2H_2+O_2\rightleftarrows 2H_2O(K_{O_2}=[H_2O]^2/[H_2]^2[O_2]),$$

the values of K_{O_2} are given in the same table and graph. K_{O_2} is smaller than K_{OH} up to about 2600°K where the two curves intersect. This means that below this limit the dissociation into hydroxyl is less than that into oxygen, but above this limit the hydroxyl dissociation prevails.

TABLE II. Equilibrium constants K_{OH} and K_{O_2}.

T°K	$\log_{10} K_{OH}$	$\log_{10} K_{O_2}$
400	67.62	58.53
600	42.81	37.30
800	30.35	26.60
1000	22.80	20.14
1100	20.07	17.79
1200	17.78	15.82
1300	15.85	14.15
1400	14.18	12.71
1500	12.74	11.46
2000	7.69	7.10
2500	4.66	4.47
3000	2.63	2.71

V. PROBABILITIES OF TRANSITION

In the measurement of the probabilities of transition ("f values") of the various OH lines given by O. Oldenberg and F. F. Rieke,[5] the greatest uncertainty was caused by the computation of the equilibrium. The present results permit a more accurate computation. It leads to the conclusion that the f values published (Table II of reference 5) must be multiplied by 4.2.

From the comparison with related reactions known from thermochemistry or band spectra (see Section IV, A), it is evident that their energies are known with higher accuracy. Considering the importance of the H_2O molecule, a more accurate determination would be desirable. But it is difficult to suggest improvements in the complicated method. The largest error comes from the matching of absorption lines. Therefore the results would be improved by the application of a still more powerful spectrograph which would give evidence of the contour of each single absorption line and make the application of the densitometer more reliable. Unfortunately, Fabry-Pérot plates are not well applicable to absorption spectra because they require a background continuous over the width of the absorption line, yet narrow enough so that adjacent orders of interference do not overlap.[3] As the second order of the 21-foot grating is not far below the requirements, a larger concave grating (35-foot) may be expected to help; but it would necessitate a more intense source of a continuous background.

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Vapor Pressures, Heats of Vaporization, and Entropies of Some Alkali Halides*

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Vapor pressures of crystalline KCl, KBr, KI, and NaCl have been measured in the pressure range of 10^{-1} to 10^{-7} mm by a surface ionization method. Heats and entropies of vaporization are calculated from the data. The heats of vaporization at 0°K and entropies at 298°K are also calculated. From the data, saturated KCl vapor is shown to be less than 2 percent associated at 800°K and the heat of dissociation of $(KCl)_2$ is shown to be less than 47 kcal.

INTRODUCTION

THE purpose of these experiments was to measure the vapor pressures of some alkali halides over their crystals, and to calculate heats of vaporization from the data. Previous experimenters,[1–6] with two exceptions,[7,8] have only measured the vapor pressure of the molten salt. To measure accurately the extremely low pressures at the high temperatures involved, a combination of Knudsen's effusion method[9] with Langmuir's positive ion method[10] was employed.

Salt molecules escaping into a vacuum from a small hole in an oven at known temperature were allowed to fall on an incandescent tungsten filament whose surface was covered with a layer of adsorbed oxygen to increase the work function. Complete dissociation of the salt and ionization of the alkali metal took place at the surface of the filament, according to the equation

$$MX \rightarrow M^+ + X + e^-_{(\text{in metal})}, \qquad (1)$$

and the escaping metal ions were then collected and their number measured electrically. Use of the well-known formula for the number of gas molecules striking a surface allowed calculation of the salt vapor pressure in the oven.

APPARATUS

The apparatus is shown in Fig. 1. Salt crystals placed in the oven A were heated by coils of Nichrome wire B wound on the quartz tube C. The whole was enclosed by a silver housing D. The oven A was a 4×1.5 cm polished silver tube and cover of 0.1-cm wall thickness. Salt vapor escaped from the oven through the hole E, of 0.165-cm diameter, which was finished with knife-sharp edges, and fell on the 0.02-cm tungsten filament F. Stray molecules were eliminated and the beam defined by apertures in the radiation shield G and collector ring H. The beam could be interrupted by a magnetically operated shutter at I. The ions leaving a known length (2.2 cm) of filament were collected by H; the remainder were collected by the guard rings J.

Current for heating the filament was supplied by storage batteries K. The voltage drop in the filament could be measured by means of potential leads soldered to its ends. The temperature of the filament was calculated from the tables of Langmuir and Jones.[11]

Current for heating the oven could be taken from a vacuum-tube voltage stabilizer[12] when desired. In this way the oven temperature could be held constant within 0.5°C for several hours.

The collector and guard rings were attached to

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† Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Columbia University.

[1] H. von Wartenburg and Ph. Albrecht, Zeits. f. Electrochemie **27**, 162 (1921).

[2] H. von Wartenburg and H. Schultz, Zeits. f. Electrochemie **27**, 568 (1921).

[3] O. Ruff and S. Mugdan, Zeits. f. anorg. allgem. Chemie **117**, 161 (1921).

[4] E. F. Fiock and W. H. Rodebush, J. Am. Chem. Soc. **48**, 2522 (1926).

[5] S. Horiba and H. Baba, Bull. Chem. Soc. Japan **3**, 11 (1928).

[6] C. G. Maier, Tech. Paper 360, U. S. Bur. Mines, Washington (1925).

[7] V. Deitz, J. Chem. Phys. **4**, 575 (1936).

[8] J. E. Mayer and I. H. Wintner, J. Chem. Phys. **6**, 301 (1938).

[9] M. Knudsen, Ann. d. Physik **47**, 697 (1915).

[10] I. Langmuir and J. B. Taylor, Phys. Rev. **51**, 753 (1937).

[11] I. Langmuir and H. A. Jones, Gen. Elec. Rev., pp. 310–319 (June, 1927).

[12] H. K. Hughes and R. J. Hurka, Rev. Sci. Inst. **6**, 289 (1935).

the same potential source L, but the connection from the collector ring was through the galvanometer M (of 1.6×10^{-10} amp./div. sensitivity). The galvanometer was recalibrated after each run.

The temperature of the oven was measured with a silver-constantan thermocouple N. This thermocouple was frequently compared with a platinum-rhodium couple which had been standardized at the freezing points of Bureau of Standards samples of tin, zinc, and aluminum. No significant variation in the characteristics of the silver-constantan couple was found throughout its use. The hot junction of the couple was welded to a silver plug screwed into the end of the oven. The cold junction O was kept in a bath of crushed ice and water, and the e.m.f. was measured with a Leeds and Northrup type K potentiometer P. The leads were led through the wall of the apparatus by capillary tubes sealed with "Picein" cement.

All other leads were introduced by tungsten to glass seals. Metal parts other than those specifically described were made of nickel. Outgassing of the collector and guard rings was accomplished by heating a few coils of Nichrome wire (not shown in the figure) on the filament assemblage

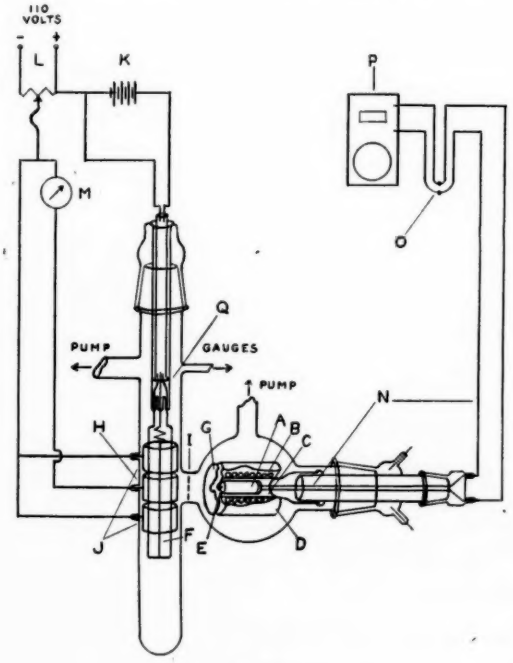

FIG. 1.

to incandescence. Since the rings did not make contact with the glass envelope except through their leads, they could be readily heated by radiation.

The filament and oven assemblies were introduced into the glass envelope by means of ground glass joints and sealed with Apiezon "L" grease.

The system was evacuated by a single-stage mercury diffusion pump with mechanical backing. Residual gas pressure was measured by McLeod and improved ionization[13] gauges. Pumping speed was approximately 1.5 liters per second, and the limiting vacuum (after a few days' evacuation) with filament and oven hot was of the order of 5×10^{-7} mm. Mercury vapor was eliminated by means of cold traps. Liquid air could also be placed in the well at Q to remove condensible material from the filament chamber.

PROCEDURE

The procedure was as follows. C.P. salt was recrystallized twice and dried by heating to about 400°C in air. Meanwhile the apparatus was evacuated and outgassed. When the outgassing was complete, the apparatus was opened, about a gram of salt placed in the oven, and the apparatus evacuated again as quickly as possible. The oven temperature was raised to the desired point and kept there until the pressure of the residual gases dropped below 5×10^{-5} mm.

The electron emission and temperature of the filament were then measured to make sure that the work function of the surface was well above the ionization potential of the metal of the salt being investigated. If it was not, a small amount of air (approx. 10^{-4} mm) was introduced by means of a capillary and the filament heated to 1400°K to coat it with a layer of oxygen. Usually there was enough oxygen in the residual gases to keep the work function high.

Sufficient potential was put on the collector and guard rings to overcome space charge. The galvanometer was set at zero with the filament lit but with the shutter I closed in order to eliminate small stray currents. When the shutter was opened the resulting galvanometer deflection was assumed to be due entirely to alkali ions from the salt molecules.

[13] R. S. Morse and R. M. Bowie, Rev. Sci. Inst. **11**, 91 (1940).

The vapor pressure was calculated from the equation

$$P=(N_0\cdot R^2(2\pi mkT)^{\frac{1}{2}}/r^2\cdot A\cdot F)i, \qquad (2)$$

where P is the pressure, N_0 Avogadro's number, R the distance from the filament to the oven, m the mass of the molecule, k Boltzmann's constant, T the absolute temperature of the oven, r the radius of the hole in the oven, A the area of the plane projection of the filament intercepting the molecules, F the Faraday, and i the measured ion current.

A correction for the scattering of the molecules in the beam by the residual gas was applied. This was determined by measuring the ion current at constant oven temperature while varying the residual gas pressure and extrapolating to zero pressure. The correction never amounted to more than 15 percent, and was reproducible within a few percent.

For measuring very low pressures a different procedure was employed. Salt vapor was allowed to condense on the cold filament for a measured length of time. The filament was then flashed, and the amount of salt evaporating measured by the ballistic kick of the galvanometer. By comparing the ballistic reading with the steady current reading at several temperatures at which the two methods could both be used, a calibration constant for converting ballistic throw into vapor pressure was obtained. This agreed within the experimental error with that calculated from the galvanometer constants, assuming complete ionization of the salt condensed on the filament, as long as the amount of salt on the surface corresponded to less than about 5 percent of a monomolecular layer.

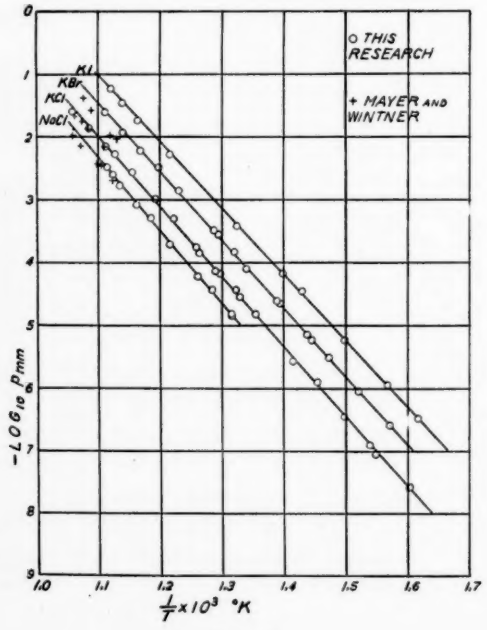

FIG. 2.

TABLE I. Experimental data.

KCl $-\log_{10} p_{mm}$	KCl $\frac{1000}{T}$ (°K)	KBr $-\log_{10} p_{mm}$	KBr $\frac{1000}{T}$ (°K)
1.60	1.058	1.60	1.111
1.86	1.085	1.93	1.140
2.15	1.112	2.49	1.198
2.26	1.127	2.85	1.230
2.57	1.155	3.49	1.287
2.98	1.193	3.55	1.294
3.30	1.222	3.83	1.320
3.75	1.258	4.10	1.340
3.83	1.263	4.61	1.389
4.13	1.290	4.65	1.393
4.17	1.297	5.14	1.437
4.23	1.301	5.22	1.445
4.44	1.321	5.50	1.471
4.54	1.328	6.04	1.520
4.82	1.355	6.59	1.570
5.57	1.415		
5.88	1.454		
6.45	1.497		
6.90	1.538		
7.04	1.548		
7.57	1.603		

KI $-\log_{10} p_{mm}$	KI $\frac{1000}{T}$ (°K)	NaCl $-\log_{10} p_{mm}$	NaCl $\frac{1000}{T}$ (°K)
		2.47	1.115
1.22	1.120	2.60	1.124
1.45	1.139	2.77	1.135
1.73	1.163	2.78	1.136
2.28	1.215	3.08	1.161
3.40	1.323	3.29	1.185
4.17	1.399	3.70	1.215
4.45	1.429	4.22	1.261
5.24	1.496	4.43	1.284
5.93	1.566	4.81	1.316
6.48	1.617	4.85	1.316

EXPERIMENTAL RESULTS

The data are given in Table I and are plotted in Fig. 2. Data from an earlier paper[8] are also plotted, but were not used in the calculations.

We would expect the data to be described by equations of the form

$$\log_{10} p_{mm}=C-A(1000/T)+2\log_{10}(1000/T) \qquad (3)$$

where the 2 log $(1000/T)$ term arises from the

difference of heat capacities between gas and crystal. Examination of data compiled in the Landolt-Börnstein Tabellen and calculation of the heat capacity of the gas by standard methods[14] show that this difference is approximately $2R$ in the temperature range from 500°K to 1000°K. The exact value of $2R$ is not of much importance since it represents only a small correction term.

The experimental points are well fitted by equations of this form. The constants A and C were evaluated from the data by the method of least squares and are given in Table II. The curves in Fig. 2 are plots of Eq. (3) using these constants.

Heats of vaporization at 800°K were evaluated from Eq. (3) by means of the Clapeyron-Clausius relation

$$d \ln p/d(1/T) = -(\Delta H/R) \tag{4}$$

and are tabulated in Table III.

DISCUSSION OF THE METHOD

For success, the positive ion method demands that the dissociation and ionization of the salt on the filament be practically complete. The ionization of the metal atom is the result of a competition between it and the filament surface for its valence electron. If the electron affinity of the surface, as measured by its "work function," is much higher than that of the atom, the atom is invariably ionized. High work functions are obtained by allowing a monomolecular layer of oxide to form on the surface, but this layer strips off when the temperature becomes too high.

On the other hand, if the temperature is too low, dissociation of the salt will not be complete. It is desirable, therefore, to make a quantitative analysis of the conditions under which the degree of dissociation α will be nearly unity and at the same time the ratio of metal ions to atoms, $r = p_{M^+}/p_M$ will be large (where p_{M^+} and p_M are the pressures of the respective species). The size of α and r are controlled by two equilibrium constants which we will now discuss.

The first equilibrium constant is that of the reaction

$$M \rightarrow M^+ + e^-, \tag{5}$$

$$K_I = (p_{M^+} \cdot p_e)/p_M = \exp(-\Delta F^0/RT), \tag{6}$$

$$\Delta F^0 = E_i - T(S_{M^+}{}^0 - S_M{}^0) + F_e{}^0, \tag{7}$$

where E_i is the energy of ionization of the metal atom, $F_e{}^0$ the standard free energy of the electrons, and $S_{M^+}{}^0$, $S_M{}^0$, the standard entropies of the ions and atoms, respectively.

Now the supply of electrons from the filament is inexhaustible, so we may consider their pressure to be a constant (at constant temperature) and remove it from the equilibrium constant. When we do this we obtain the new constant

$$K_I' = r = \frac{p_{M^+}}{p_M} = \exp - \frac{(E_i + F_e{}^0 + RT \ln p_e)}{RT} \cdot \exp \frac{(S_{M^+}{}^0 - S_M{}^0)}{R}. \tag{8}$$

The quantity $F_e{}^0 + RT(\ln p_e)$ is the free energy of the electrons, which is approximately the negative of the quantity commonly called the "work function" of the filament surface,* and which is

TABLE II. Constants to be used in Eq. (3).

Salt	A	C
KCl	11.879	11.006
KBr	11.543	11.141
KI	11.263	11.277
NaCl	12.288	11.093

TABLE III. Heats of sublimation at 800°K and at 0°K.

Salt	ΔH_{800} (kcal.)	ΔH_0 (kcal.)
KCl	51.15±0.25	53.50±0.4
KBr	49.61±0.22	52.40±0.4
KI	48.33±0.27	51.41±0.5
NaCl	53.02±0.47	55.32±0.5

[14] J. E. Mayer and M. Goeppert-Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940).

* Note: Some confusion exists in the literature concerning the exact meaning of the term "work function." The quantity here used, the negative of the free energy of the electrons, can be shown (reference 14) to be the numerator of the exponent of the expression

$$i = 120.1 T^2 \exp(-e\varphi/kT), \tag{N-1}$$

where i is the electron emission in amperes per square centimeter. This equation is derived assuming only that the electrons are a perfect gas with a doubly degenerate internal quantum state (resulting from spin), and that the reflection coefficient of the surface for electrons is zero.

In most literature, however, the "work function" is defined as the numerator of the exponent of the empirical equation

$$i = AT^2 \exp(-e\varphi/kT), \tag{N-2}$$

where the coefficient A has a value in general different from 120.1. For clean tungsten, for example, A has the value 60.2 (reference 11). The difference can be reconciled by making the φ of the first equation slightly temperature dependent.

For our purposes the difference is not important.

TABLE IV. Calculated dissociation constant of KCl as a function of temperature.

T (°K)	$-\log_{10} K_{II}'$ (mm)
1400	6.1
1500	5.2
1600	4.4
1700	3.7

nearly independent of temperature. With $S_{M^+}{}^0 - S_M{}^0 = R \ln 2$, Eq. (8) now takes the final well-known form

$$r = 1/2 \exp (\epsilon\varphi - E_i)/RT, \tag{9}$$

where φ is the work function of the filament surface.

In the first place, we see that the extent of ionization depends on the difference between the work function of the surface and the ionization potential of the alkali, as predicted. Calculation shows that for 99 percent ionization of potassium at 1500°K, the work function must be 5.01 volts or higher, for sodium 5.81 volts.

The second equilibrium constant which we must consider is that of the reaction

$$MX \rightarrow M^+ + X + e, \tag{1}$$

$$K_{II} = \frac{p_{M^+} \cdot p_X \cdot p_e}{p_{MX}} = K_{II}' \cdot p_e. \tag{10}$$

With the same symbols and E_d, the energy of dissociation of the gas molecule, this can be shown to be

$$K_{II}' = \exp (S_X{}^0 + S_M{}^0 - S_{MX}{}^0 - R)/R \cdot \exp (\epsilon\varphi - E_d - E_i)/RT. \tag{11}$$

If α, the fraction dissociated, is nearly unity, the relation

$$\alpha = 1 - [(p_{MX \text{ initial}})/K_{II}'] \tag{12}$$

holds approximately. K_{II}' may be calculated if the thermodynamic functions in Eq. (11) are evaluated by the statistical methods used elsewhere in this paper. This was done at several temperatures for potassium chloride using $\varphi = 5.20$ volts. The results are given in Table IV.

Taking the extreme case, it is seen that at the highest measured pressure of KCl (corresponding to $\log p_{mm} = -5.4$ at the filament surface) $\alpha = 98$ percent at 1700°K. At lower pressures α is of course still nearer unity.

It was found possible to maintain work functions of 5 to 6 volts up to about 1800°K, so that there should be a region in the neighborhood of 1700° within which dissociation and ionization are complete. Experimentally, this region should appear as a flat maximum in the plot of ion current (at constant oven temperature) against filament temperature. Such a plot for KCl is shown in Fig. 3, and the expected maximum is found. This behavior is like that observed by other workers.[15] Similar maxima were observed for the other salts used, and the measurements were always made at filament temperatures lying within this region.*

In this and previous work of the kind it has been assumed that every halide molecule striking the surface sticks long enough to reach thermal and chemical equilibrium; i.e., the accommodation coefficient of the surface is assumed to be unity. Such as assumption has been shown to be correct for caesium on tungsten,[16] hydrogen on tungsten,[17] and probably true for chlorine[18] and bromine[19] on tungsten. On the other hand, it is

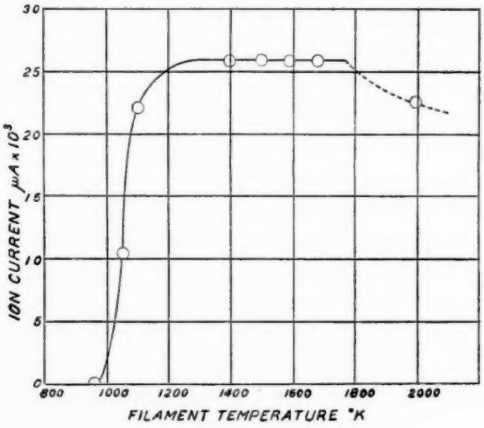

FIG. 3.

[15] T. E. Phipps, M. J. Copley, and J. O. Hendricks, J. Chem. Phys. 5, 868 (1937).

* Note: A direct experimental check of Eq. (11) was impossible because at the lower temperatures at which incomplete dissociation occurred the electron emission, from which the work function was determined, was too small to measure.

[16] I. Langmuir and J. B. Taylor, Phys. Rev. 44, 423 (1933).

[17] P. M. Doty, J. Chem. Phys. 11, 557 (1943).

[18] K. J. McCallum and J. E. Mayer, J. Chem. Phys. 11, 56 (1943).

[19] P. M. Doty, Thesis, Columbia University, 1944.

TABLE V. Entropies in cal./deg.

Salt	(S_{gas}°/R) 800°K	$-\ln p_{mm}$ 800°K	S_{gas} 800°K	ΔS_{vap} 800°K	S_{cryst} 800°K	S_{cryst} 800°K $-S_{cryst}$ 298°K	S_{cryst} 298°K	S_{cryst} 298°K (from the literature)
KCl	39.92	8.41	95.98±0.14	63.94±0.38	32.04±0.40	12.69±0.2	19.35±0.5	19.75±0.06[a]
KBr	41.24	7.12	96.04± .14	62.01± .34	34.03± .37	13.16± .3	20.87± .5	22.6 ± .5[b]
KI	42.15	6.01	95.65± .14	60.41± .39	35.24± .41	13.01± .5	22.2 ± .7	24.1 ± .5[b]
NaCl	38.99	9.38	96.06± .14	66.28± .67	29.78± .67	12.77± .2	17.0 ± .8	17.3 ± .5[c]

[a] From heat capacity measurements. Cf. reference 21.
[b] From reststrahlen. K. K. Kelley, U. S. Bur. Mines Bull. 350 (1932).
[c] From reststrahlen supported by some heat capacity data. Kelley, reference *b*.

not true for methyl chloride[17] and hydrocarbons on tungsten and other metals. In general, accommodation coefficients of unity seem to be obtained for those gases and vapors which are chemi-adsorbed on the surface, whereas in cases in which only van der Waals forces are active very small accommodation coefficients are obtained. Since the image forces between a strong dipole such as an alkali halide molecule and the surface of a metal should be quite large, we might reasonably expect to find an accommodation coefficient close to unity. Also, the agreement between the values of the vapor pressure obtained by allowing the salt to fall on a cold (300°K) filament with subsequent flashing and the values obtained with the salt falling on a filament at 1700°K shows an independence of the accommodation coefficient of temperature that would be hard to explain if it were other than unity.

CRYSTAL ENTROPIES

The entropy of vaporization is related to the heat of vaporization by

$$\Delta H = T\Delta S. \tag{13}$$

The absolute entropy of the gas can be calculated accurately from spectroscopic data, and the heat capacity of the crystals above room temperature is known, so that sufficient information is available to calculate the entropy of the crystal at room temperature. The calculation of the gas entropy was performed using the usual statistical-mechanical equations[14] (including a small correction for rotational stretching and anharmonicity) and data from the compilation by Herzberg.[20] The heat capacities of the crystals above room temperature were taken from the Landolt-Börnstein Tabellen. A short extrapolation was necessary for KBr and a long one for KI.

The calculations are summarized in Table V.

DIMERIZATION OF THE VAPOR

We have assumed that there is no dimerization in the saturated salt vapor. It is possible to show, at least for KCl, that this assumption is correct by comparing the crystal entropy as calculated above with the one calculated from very good heat capacity data (from 15°K to room temperature) by Southard and Nelson.[21] The two entropies agree within the experimental error, with ours, calculated assuming no association, being slightly lower. The presence of appreciable association would lower the calculated entropy of the gas and destroy the agreement of the two values. A detailed calculation (see Appendix) shows that for saturated KCl vapor at 800°K the fraction associated is certainly less than 2 percent and probably less than 0.3 percent. This is in agreement with the conclusion of Deitz,[7] who found saturated KCl vapor to be less than 10 percent associated.

The probable error introduced in the heat of vaporization by association can also be shown to be less than 0.1 kcal. (see Appendix). Because of their similar properties, it was assumed that the amount of association in the vapors of the other salts was likewise negligible. In view of the unreliability of the entropy values found in the literature for these salts no direct calculation of the degree of association was attempted.

HEAT OF VAPORIZATION AT ABSOLUTE ZERO

The heat content of the vapor was calculated statistically in the same manner as the entropy.

[20] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939).

[21] J. C. Southard and R. A. Nelson, J. Am. Chem. Soc. **55**, 4865 (1933).

The heat content of the crystal was obtained by integrating the available heat capacity data. The difference of these two quantities added to the heat of vaporization at 800°K gives the heat of vaporization at absolute zero. The results are tabulated in the last column of Table III.

ERRORS

The precision measure of the heats of vaporization is the square root of the sum of the squares of the following individual errors: the "probable error" in the least-squaring of the experimental points; a systematic error in temperature measurement of possibly 0.4 percent; a possible systematic error in the logarithm of the vapor pressure (resulting mainly from incompleteness of ionization) amounting to 0.2 percent for the potassium salts and 0.4 percent for NaCl.

The entropies of vaporization contain an additional possible 0.4 percent error from the temperature.

The precision measure of the entropies of the vapor is the square root of the sum of the squares of the errors resulting from probable errors in temperature, pressure, fundamental frequency (±1 percent), and moment of inertia (±3 percent).

APPENDIX

Calculation of the Extent of Association in KCl Vapor at 800°K

The outline of the method is this: We calculate the entropy of a gaseous mixture of monomer (KCl) and dimer $(KCl)_2$ and compare with the experimental entropy of the vapor. This allows us to set a maximum value for the extent of association. Using a thermodynamic equation connecting the extent of association, entropy, and heat content of the crystal and saturated vapor we then may calculate maximum and minimum values for the heat of association and the maximum error in the heat of vaporization of the monomer.

We shall use the following symbols to save space: S_2 and ΔH_2 for the entropy and heat of vaporization per mole of the dimer, S_1 and ΔH_1 for the same quantities per mole of monomer, and S_c the entropy of the crystal, all at 800°K.

Entropy of the Dimer

A rough calculation using only electrostatic terms shows that a square configuration with like atoms at opposite corners is energetically the most stable form of the molecule. In view of the small difference between the interatomic distance in the monomer (2.79A) and in the crystal (3.14A), we shall assume that the interatomic distance in the dimer is the same as in the monomer.

Using this model, the entropy due to rotation is easily calculated.[14]

$$S_{2\,\mathrm{rot}}=(\tfrac{3}{2})S_{1\,\mathrm{rot}}-(\tfrac{3}{4})R\ln 2+(\tfrac{1}{2})R\ln\pi. \qquad \text{(A-1)}$$

The translational entropy at standard pressure (one millimeter) is

$$S^0{}_{2\,\mathrm{trans}}=S^0{}_{1\,\mathrm{trans}}+(\tfrac{3}{2})R\ln 2. \qquad \text{(A-2)}$$

The vibrational entropy is less easily calculated since the frequencies are unknown. An inspection of the normal modes of vibration shows, however, that of the six, five should have approximately the same frequency as the monomer, while the sixth, the "bending" mode, should be lower by a factor of perhaps ten. The vibrational entropy is then

$$S_{2\,\mathrm{vib}}=6S_{1\,\mathrm{vib}}+R\ln 10(\pm 3R). \qquad \text{(A-3)}$$

Inserting numerical values we obtain 114±6 cal./deg. for the entropy per mole of the dimer at 1 mm pressure and 800°K.

Entropy of a Saturated Mixture of Monomer and Dimer

If x is the fraction of monomer associated, the entropy per mole of monomer in the saturated vapor will be (from Table V)

$$S_1=95.98\pm 0.14-R\ln(1-x). \qquad \text{(A-4)}$$

The natural logarithm of the saturated vapor pressure is −8.41, so that the entropy of the dimer in the saturated vapor will be

$$S_2=S_2{}^0-R\ln p_2=131-R\ln(x/2). \qquad \text{(A-5)}$$

The entropy of the mixture will be

$$S=S_1(1-x)+S_2(x/2)=95.98\pm 0.14-30.5x \\ -R(1-x)\ln(1-x)-R(x/2)\ln(x/2). \qquad \text{(A-6)}$$

The experimental entropy (from the values in Table V) is 96.38±0.5.

It is seen that x must be small. Exactly how small to take it is a matter of taste; we prefer to set 0.02 as an upper limit with the probable value not greater than 0.003. We have assumed at this point that the presence of association does not appreciably affect the heat and hence the entropy of vaporization. This assumption will now be justified.

Error in the Heat of Vaporization due to Association

The quantity which was directly measured was the number of potassium atoms contained in the vapor molecules which hit a unit area. If we represent this number by Z_m, and the pressure calculated from it by p_m, we have

$$Z_m=\frac{p_m}{(2\pi m_1 kT)^{\frac{1}{2}}}=Z_1+2Z_2=\frac{p_1}{(2\pi m_1 kT)^{\frac{1}{2}}}+\frac{2p_2}{(2\pi m_2 kT)^{\frac{1}{2}}}. \qquad \text{(A-7)}$$

The fraction associated, x, is $2p_2/p_1$, and $m_2=2m_1$, so that

$$p_1=\frac{p_m}{1+(\sqrt{2}/2)x} \tag{A-8}$$

$$\frac{\partial \ln p_1}{\partial(1/T)}=\frac{\partial \ln p_m}{\partial(1/T)}-\frac{\sqrt{2}}{2}\frac{\partial x}{\partial(1/T)} \quad \text{(if } x \text{ is small)} \tag{A-9}$$

$$\Delta H_1=\Delta H_m+R\frac{\sqrt{2}}{2}\frac{\partial x}{\partial(1/T)}. \tag{A-10}$$

The fraction associated, x, can be shown to obey the equation

$$x=2p_2/p_1=2\exp\{[(S_2^0-S_1^0-S_e^0)/R] -[(\Delta H_2-\Delta H_1)/RT]\} \tag{A-11}$$

$$\frac{\partial x}{\partial(1/T)}=-x(\Delta H_2-\Delta H_1)/R. \tag{A-12}$$

If we insert numerical values in Eqs. (A-10), (A-11), and (A-12), using $x=0.02$ and $S_2^0=114\pm6$, we find the error in ΔH_1 to be

$$0<\left[\frac{\sqrt{2}}{2}x(\Delta H_2-\Delta H_1)\right]<0.2 \text{ kcal.} \tag{A-13}$$

If we use $x=0.003$, we find the error to be

$$0<\left[\frac{\sqrt{2}}{2}x(\Delta H_2-\Delta H_1)\right]<0.05 \text{ kcal.} \tag{A-13a}$$

It is interesting to note that we are also able by Eq. (A-11) to set an upper limit on the heat of association (using $x=0.02$):

$$(KCl)_2\rightarrow 2KCl, \quad \Delta H<47 \text{ kcal. (at 800°K).} \tag{A-14}$$

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The Reaction of Hydrogen Atoms with Acetylene*

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An investigation has been made of the reaction between hydrogen atoms and acetylene. With the large hydrogen atom concentrations produced in the discharge tube, catalytic recombination of hydrogen atoms occurs but no hydrogenated products could be detected. With small hydrogen atom concentrations resulting from mercury photosensitization, ethane and butane are produced together with a partially hydrogenated polymer. The results are discussed from the point of view of the elementary reactions involved and it is concluded that ethyl and vinyl radicals play an important part in the reaction.

INTRODUCTION

IN a previous paper[1] on the mercury photosensitized polymerization of acetylene it was concluded that hydrogen atoms and C_2H radicals are probably produced in the initial step and that the polymerization is sensitized by these primary products. In an attempt to throw further light on the problem, the present paper is devoted to an investigation of the action of hydrogen atoms on acetylene.

This has already been done by a number of workers who produced hydrogen atoms either by a discharge tube[2–5] or by mercury photosensitization.[6] In the case of the discharge-tube method it was found that although acetylene catalyzed the recombination of hydrogen atoms, no products other than hydrogen and acetylene could be detected. However, if deuterium atoms were used[5] deuterization of acetylene took place with an activation energy of less than 5 kcal. In order to explain the rapid exchange as well as atom recombination, Geib and Steacie[5] suggested the alternative mechanisms

$$\begin{aligned} D+C_2H_2&=C_2H_2D,\\ D+C_2H_2D&=C_2HD+HD, \text{ etc.,}\end{aligned} \tag{I}$$

and

$$\begin{aligned} D+C_2H_2&=C_2H+HD,\\ D+C_2H&=C_2HD, \text{ etc.}\end{aligned} \tag{II}$$

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[1] D. J. Le Roy and E. W. R. Steacie, J. Chem. Phys. **12**, 117 (1944).

[2] K. F. Bonhoeffer and P. Harteck, Zeits. f. physik. Chemie **139**, 64 (1928).

[3] H. v. Wartenberg and G. Schultze, Zeits. f. physik. Chemie **B2**, 1 (1929).

[4] K. H. Geib and P. Harteck, Ber. **66**, 1315 (1933).

[5] K. H. Geib and E. W. R. Steacie, Zeits. f. physik. Chemie **B29**, 215 (1935). Trans. Roy. Soc. (Canada) III, **29**, 91 (1935).

[6] J. R. Bates and H. S. Taylor, J. Am. Chem. Soc. **49**, 2438 (1927).

TABLE I.

Temperature	C_2H_2	H_2	Time	$-\Delta P$	$-\Delta H_2$	$-\Delta C_2H_2$	Gaseous products
25°C	22 mm	396 mm	45 min.	— mm	— mm	8.2 mm	1.3 mm
25	22	400	45	15	—	11.4	1.5
25	22	403	45	10	4.0	6.8	0.9
200	22	404	15	19	11	9.8	1.9
200	22	400	15	16.5	11	7.1	1.6
200	22	403	15	20	10	12.2	2.2
200	22	418	15	17	7.5	11.9	2.4
200	22	401	15	15	9	7.6	1.6
300	22	404	15	32	19	18.4	5.4
300	22	403	15	31	19	16.2	4.2
300	22	399	15	25	16	12.2	3.2

In other words, the experimental results could be explained on the assumption that the primary step consisted of the formation of either the vinyl radical or the ethynyl radical. At the present time there is no method of deciding between the two mechanisms.

Bates and Taylor[6] have reported experiments in which they subjected hydrogen-acetylene mixtures to mercury photosensitization. The reaction appeared to be largely one of polymerization, since they were unable to detect any saturated products. However, their hydrogen pressure was not high enough to prevent appreciable quenching by acetylene so that hydrogenation, if it occurred, was probably masked by a considerable amount of straight polymerization.

Disregarding the work of Bates and Taylor, which was of course largely of an exploratory nature, we are left with the problem of trying to explain the absence of hydrogenation in the presence of hydrogen or deuterium atoms. It consequently seemed desirable to re-investigate not only the mercury photosensitized hydrogenation but also the reaction of hydrogen atoms produced in a discharge tube, in the hope that it might be possible to find hydrogenated products which had previously escaped detection.

A. HYDROGEN ATOMS PRODUCED IN THE DISCHARGE TUBE

The discharge tube was of the usual type and was operated by a 5000-volt $2\frac{1}{2}$-kva transformer. Using a hydrogen flow rate of 75 cc per min. at atmospheric pressure and an operating pressure of 0.4 mm the contact time was 0.5 sec. A Wrede gauge[7] indicated an atom concentration of approximately 35 percent. Acetylene could be admitted to the reaction vessel at either 6.5 or 1.6 cc (at atmospheric pressure) per min. The procedure was to start with an accurately determined volume of acetylene and transfer it to a vessel where it could be admitted to the reaction vessel at a constant rate by raising a mercury levelling bulb. When most of the acetylene had been brought into the hydrogen atom stream in this way, the discharge was stopped and the remaining acetylene pumped through the apparatus and combined with the products.

To avoid loss of any ethane or ethylene which might be produced, the products were not condensed in the usual way, but after passing through the four-stage mercury diffusion pump they were condensed in a trap filled with silica gel and cooled with liquid air. The hydrogen which passed through this trap was pumped off by a Megavac pump. Steacie and Phillips[8] used silica gel in this way and found that they could separate methane from hydrogen with high efficiency.

The catalysis of the recombination of hydrogen atoms by acetylene was investigated by inserting two adjacent thermocouple wells in the lower part of the reaction vessel. One of these was poisoned, as was the rest of the apparatus, by phosphoric acid. The other was wound with a few turns of silver wire and, by measuring the difference in temperature between the two wells, it was possible to get an indication of the hydrogen atom concentration from the rate of recombination on the silver wire. On admitting acetylene the temperature immediately began to fall and the rate of temperature decrease for a given temperature was the same as it was for the discharge shut off, i.e., for no atoms present, indicating complete removal of hydrogen atoms in the presence of acetylene.

The volume of gaseous products collected at the end of a run was found to agree with that originally taken within about one percent and chemical analysis showed no gas other than acetylene. It would appear, then, that although acetylene will catalyze the recombination of hydrogen atoms and be almost completely deuterized if deuterium atoms are used,[5] no hydrogenation occurs under these conditions.

[7] E. Wrede, Zeits. f. Instrumentenk. **48**, 201 (1928); P. Harteck, Zeits. f. physik. Chemie **A139**, 98 (1928).

[8] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. **4**, 461 (1936).

TABLE II.

25°C

C_2H_2	H_2	Time	$-\Delta P$	$-\Delta H_2$	$-\Delta C_2H_2$	"C_2H_4"	C_2H_6	C_4H_{10}
0.35 mm	4.28 mm	22 min.	0.13 mm	0.098 mm	0.057 mm	0.003 mm	0.018 mm	0.002 mm
0.37	4.15	45	.24	.182	.126	.004	.031	.012
0.36	4.07	120	.48	.307	.267	.004	.057	.025

B. HYDROGEN ATOMS PRODUCED BY MERCURY PHOTOSENSITIZATION

The first series of runs was done using a quartz annular cell and the full radiation of the lamp.[9] The results are shown in Table I.

Column one gives the temperature; two, the original pressure of acetylene; three, the original pressure of hydrogen; four, the duration of the run; five, the observed pressure decrease; six, the amount of hydrogen used up expressed in mm; seven, the amount of acetylene used up also in mm; and eight, the amount of gaseous products formed.

The observed pressure decreases at 300°C exceed the initial pressure of acetylene, indicating that considerable hydrogenation took place. This was also observed at room temperature when runs of long duration were made. It is also apparent from the table that the rate of hydrogenation increased considerably with temperature.

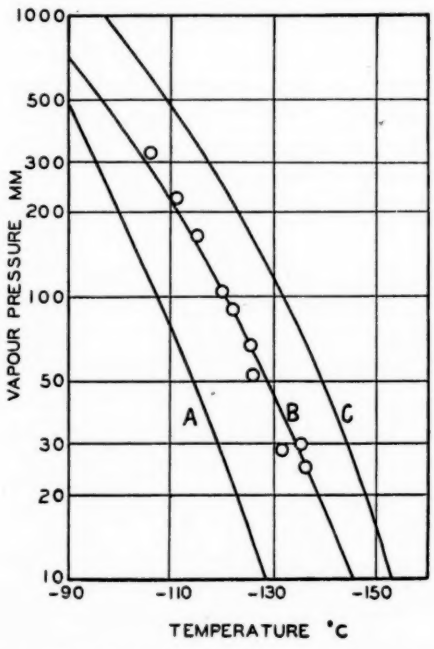

FIG. 1. The circles represent the vapor pressure of gaseous products from two runs at 25°C. The solid lines *A*, *B*, and *C* are for acetylene, ethane, and ethylene, respectively.

Analysis of the gaseous products offered some difficulty owing to their small volume. Acetylene was removed from the condensible products at the end of a run by shaking with potassium mercuric iodide. The remaining gas was collected, freed from water vapor, and measured. Its vapor pressure was then determined over a range of temperature by the method of Benson.[10] The results are shown in Fig. 1. The solid lines *A*, *B*, and *C* give the vapor pressures of pure acetylene, ethane, and ethylene, respectively. The experimental points are for two separate runs at 25°C and indicate that ethane is an important product. Further evidence in this regard is given below.

A second series of runs was made at a total pressure of about 4.5 mm and 25°C using the system previously described (Series I, reference 1). The results are given in Table II.

The first six column headings have the same significance as in Table I but in this case a more complete analysis of the gaseous products was made. After removing the hydrogen the condensible gas was collected and analyzed by means of the Blacet-Leighton apparatus.[11]

The decrease in hydrogen was calculated from the observed pressure decrease together with the volume of condensible gas. The latter was measured by compressing it into a calibrated volume by means of a mercury diffusion pump backed by a Toepler pump. It was then transferred to the gas analysis apparatus with a diffusion pump backed by an automatic Sprengel pump. Acetylene was absorbed with a potassium hydroxide-

[9] D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. **10**, 676 (1942).

[10] S. W. Benson, Ind. Eng. Chem. Anal. Ed. **14**, 189 (1942).

[11] F. E. Blacet and P. A. Leighton, Ind. Eng. Chem. Anal. Ed. **3**, 266 (1931).

mercuric cyanide bead, and ethylene with fuming sulphuric acid. The residue was analyzed by combustion and the carbon and hydrogen values agreed best on the assumption that this gas was a mixture of ethane and butane. The amounts of these products, expressed in mm, are given in the last two columns of Table II. There was such a small amount of unsaturated gas in the mixture after removing the acetylene that accurate analysis was precluded. Consequently it was merely called "C_2H_4" although there is a possibility that it was a higher olefin or even a small amount of paraffin which dissolved in the fuming sulphuric acid. The amount of this substance is given in column seven. With the exception of this "C_2H_4" the values for the other products are quite reliable because the small amount of gas needed for an analysis made it possible to do several determinations on the products of a given run.

The results of the two series are then in reasonably good agreement and point to ethane as an important product. In the latter series carbon and hydrogen balances were made on the over-all reaction and they indicated that the acetylene disappearing by processes other than the formation of "ethylene," ethane, and butane was equivalent to slightly more than the amount used up in forming these products. The empirical formula of the polymer was approximately $(C_2H_4)_x$.

It is unfortunate that "C_2H_4" was produced in such a small percentage because, while ethane and butane formation increased continuously with time, "C_2H_4" appeared to reach a constant value of 0.004 mm. This might be taken to indicate that "C_2H_4" is an intermediate in the formation of ethane and butane but the evidence is not very reliable.

DISCUSSION

The important point about this work is that while no hydrogenation occurs with the high hydrogen atom concentrations of the discharge tube it takes place readily at the low concentrations resulting from mercury photosensitization. Regardless of whether mechanism I or II of Geib and Steacie is correct it would seem to be necessary that vinyl radicals be formed before any hydrogenation can take place. This could occur by either

$$H+C_2H_2=C_2H_3 \quad (1)$$

or

$$H+C_2H_2=C_2H+H_2, \quad (2)$$

followed by

$$C_2H+H_2=C_2H_3. \quad (3)$$

The absence of hydrogenation in the discharge-tube method could then be explained on the assumption that the reaction

$$H+C_2H_3=C_2H_2+H_2 \quad (4)$$

or

$$H+C_2H=C_2H_2 \quad (5)$$

occurs much more readily in the presence of high hydrogen atom concentrations than the reactions

$$C_2H_3+H_2=C_2H_4+H, \quad (6)$$

$$C_2H_3+H_2=C_2H_5, \quad (7)$$

$$C_2H_3+H=C_2H_4, \quad (8)$$

and

$$C_2H+H_2=C_2H_3. \quad (9)$$

It is difficult to see how (8) would occur in the photosensitized experiments and not with the discharge tube unless it involved a ternary collision. And since the total pressure in the discharge-tube method was just about one-tenth of the lower pressure used in the former method, it would seem likely that (8) is not involved at all, even as a ternary reaction.

If ethylene actually is an intermediate the most likely method of formation is (6). Ethane and butane formation would then involve (10):

$$H+C_2H_4=C_2H_5, \quad (10)$$

which is known to have a small activation energy. Whether this is followed by

$$C_2H_5+H_2=C_2H_6+H, \quad (11)$$

$$2C_2H_5=C_4H_{10}, \quad (12)$$

$$2C_2H_5=C_2H_4+C_2H_6, \quad (13)$$

is open to question but it is known that butane is formed at room temperature in systems containing hydrogen, ethylene, and acetylene[12] and

[12] D. J. Le Roy and E. W. R. Steacie, J. Chem. Phys. 9, 829 (1941).

both (12) and (13) are generally conceded to have small activation energies.[13]

If ethylene is not a true intermediate the gaseous products could be accounted for by the reactions (7), (11), (12), and (13).

Polymer formation is undoubtedly sensitized by radicals for even if the mercury photosensitized polymerization in the absence of hydrogen[1] were not a free radical process, the large $H_2:C_2H_2$ ratios used in this work would largely eliminate the possibility of quenching $Hg(^3P_1)$ atoms by acetylene. Furthermore, Jungers and Joris[14] have shown that ethyl radicals will sensitize the polymerization of acetylene and while there is little direct evidence for a sensitized polymerization by vinyl radicals, the analogous reaction with ethylene has been fairly well established.[9,15,16]

[13] *Annual Tables of Physical Constants* (1942), Section 602.
[14] J. C. Jungers and G. G. Joris, Bull. Soc. Chim. Belg. **50**, 61 (1941).
[15] E. W. R. Steacie and D. J. LeRoy, J. Chem. Phys. **10**, 22 (1942).
[16] H. Habeeb, D. J. LeRoy, and E. W. R. Steacie, J. Chem. Phys. **10**, 261 (1942).

The main points in connection with the reaction between hydrogen atoms and acetylene can be summarized as follows:

(1) With high hydrogen atom concentrations hydrogenation of acetylene is prevented by

$$H+C_2H_3=C_2H_2+H \qquad (4)$$

or

$$H+C_2H=C_2H_2. \qquad (5)$$

(2) With low hydrogen atom concentrations hydrogenation does occur, with the formation of ethane and butane.

(3) The hydrogenated products can best be accounted for on the assumption that both vinyl and ethyl radicals are formed.

(4) A partially hydrogenated polymer is formed as the result of a radical sensitized polymerization of acetylene.

(5) The results lend some weight to the assumption that the mercury photosensitized polymerization of acetylene proceeds by a free radical process.

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A Molecular Theory of the Viscoelastic Behavior of an Amorphous Linear Polymer

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The kinetic theory of rubber elasticity is extended in two respects. First, the distribution of relative displacements of every chain atom is considered, not merely the distribution of relative chain-end displacements. Second, the rate of approach to elastic equilibrium, as well as the equilibrium itself, is considered. As a first approximation, it is predicted that a linear amorphous polymer will possess a distribution of elastic retardation times of the form $J(\tau)d\tau = (C \ln \tau - D)d \ln \tau$, where C and D are constants characteristic of the material.

INTRODUCTION

THE only well-established molecular theory relating to the plastoelastic properties of amorphous high polymers is the kinetic theory of long range elasticity.[1–3] This theory has proved valuable in understanding the magnitude and the temperature dependence of elastic moduli connected with configurational changes, and in the hands of Guth and James[2] has served as a quantitative tool in the study of a series of (cross-linked) elastomers. In the study of linear polymers, however, the kinetic theory has two serious shortcomings.

(1) The undue emphasis which the theory places on the separation of chain ends is acceptable only in the case of a cross-linked network, where mesh points take the place of chain ends. This emphasis corresponds to the assumption that a tensile stress acts upon a polymer molecule only through the chain ends—as though the chain ends were grasped by microscopic tweezers and pulled apart. This is justified in the case of a cross-linked polymer, since at elastic equilibrium the network bears the entire stress load, and the chains connecting the two mesh points are indeed pulled at the ends. It is never justified in the case of a linear polymer.

(2) In any case, the existing kinetic theory is purely an equilibrium treatment. It predicts an equilibrium elastic deformation in the presence of a stress, but does not yield any information concerning the transient conditions during the establishment of elastic equilibrium.

There is need for a molecular theory which eliminates these restrictions and predicts the viscoelastic spectrum of an amorphous linear polymer—i.e., the function $J(\tau)d\tau$, which gives the amount of elastic compliance* with retardation time τ in the range $d\tau$. The purpose of this paper is to lay down the general method which such a theory should follow, and to provide an explicit first approximation.

QUALITATIVE CONSIDERATIONS

The long chain molecules in an unstressed amorphous linear polymer are distributed among their possible configurations (shapes and orientations) according to the laws of statistics. Most molecules will be neither extended to maximum length nor tightly curled into balls, but will be in the statistically favored half-curled forms. Such a randomly kinked molecule will possess bends and convolutions of all sizes. There will be local kinks, of relatively short segments, bends and curls of intermediate size, and long range convolutions of the chain as a whole. When the sample is subjected to a tensile stress, this stress will act directly upon each unit of the chain, via its environment, not merely upon the chain ends. The stress tends to straighten out the molecule and orient it in the direction of the stress. A new equilibrium distribution of configurations will hold in the presence of the stress. In this new distribution, the local kinks, the intermediate curls, and the long range convolutions will all be somewhat straightened out and oriented. During the transient period when the new elastic equilibrium is being established, the local kinks will straighten out most quickly, the intermediate

[1] E. Guth and H. Mark, Monats. F. Chem. **65**, 93 (1934); Naturwiss. **25**, 353 (1937).
[2] E. Guth and H. M. James, J. Chem. Phys. **11**, 455 (1943); Ind. Eng. Chem. **33**, 1624 (1941).
[3] F. T. Wall, J. Chem. Phys. **10**, 132 (1942); **10**, 485 (1942).

* The elastic compliance is the reciprocal of the modulus.

bends more slowly, and the long range convolutions most slowly of all. This results in a certain amount of elastic compliance which attains its equilibrium value quickly and other compliance which attains its equilibrium value slowly. Superimposed upon this retarded elastic response will be the irreversible flow which results from the slippage of entire chains past each other. This flow response can be separated out and will not be considered in this paper. In the limit, this behavior appears as a continuous distribution of elastic compliance over a wide range of retardation times.

The above qualitative remarks cannot be said to constitute a working theory, since they offer no computational framework for actually deducing the viscoelastic spectrum from molecular structure. In the following section, such a computational framework will be presented.

QUANTITATIVE CONSIDERATIONS

Consider a sample of a monodisperse linear polymer, made up of N molecules, each of which contains n chain atoms. In order to specify the position of each chain atom in the sample, $3nN$ coordinates are necessary. A point in $3nN$-dimensional phase space expresses this information, and can be considered to represent a molecular configuration of the whole sample. The diffusional motion of the sample, including both the micro- and the macro-Brownian motion, can be represented by a diffusional motion of the point in phase space. Each point in phase space represents some definite macroscopic shape of the sample. In the absence of an external stress, the representative point wanders about through a region in phase space which corresponds to the "unstrained" shape of the sample. In the presence of a stress, the representative point wanders into new regions of phase space, which correspond to finite macroscopic strains. The whole problem of the plastoelastic behavior of such a material would be solved if we were able (1) to formulate and solve the equations of motion of the point in $3nN$-dimensional phase space and (2) to compute the macroscopic strain from the values of the $3nN$ coordinates. The difficulties involved are obviously very great, if the $3nN$ Cartesian coordinates of the individual chain atoms are chosen as the reference coordinates. The question arises—can a molecular configuration be described in terms of some set of parameters other than the Cartesian coordinates of the atoms, so chosen as to simplify the mathematical problem projected here?

Such a transformation of coordinates is, of course, common practice in strictly dynamical problems. The vibration and rotation of polyatomic molecules, for example, are most effectively approached in terms of the normal coordinates of the molecule. In general, the normal coordinates are complicated functions of the atomic Cartesian coordinates of the molecule. This fact, however, is more than compensated for by the simplicity of the equations of motion when expressed in terms of the new coordinates. Our problem is one of diffusion, rather than vibration, but it may still be helpful to replace the $3n$ atomic Cartesian coordinates for a given molecule by a new set of $3n$ coordinates in terms of which the diffusional motion can be more simply expressed, and more simply connected with the macroscopic strain. It should not be surprising if the new coordinates are complicated functions of the old; indeed, it would be surprising if this were not true.

In the first place, since we intend to separate out flow (irreversible displacements of whole molecules relative to each other) and consider only configurational elastic deformation (change in the distribution of molecules among shapes and orientations), the molecular phase space for each individual molecule is to be preferred to the $3nN$ dimensional phase space for the sample as a whole. In order to make an intelligent choice of the $3n$ coordinates which are to replace the Cartesian coordinates of the chain atoms, let us consider how the macroscopic configurational strain is determined by the molecular configuration of the sample. Any definite molecular configuration of the whole sample means a definite set of values of all $3nN$ atomic Cartesian coordinates, and hence a definite distribution of values of the $3n$ coordinates defining the configuration of each individual molecule. This can be represented by a density distribution function about a reference point such as an end of the chain. This density distribution is the sum of the density distributions for the individual chain atoms. We already have, from the kinetic theory of high

elasticity, an expression for the (equilibrium unstressed) density distribution of the second chain end about the first.[4]

$$ {}^{n}W_0(x, y, z) = \frac{A}{n^{\frac{3}{2}}} \cdot \exp\left[-\frac{B}{n}(x^2+y^2+z^2)\right]. \quad (1) $$

The constant A is here chosen to normalize W_0 to unity. Using this expression for the equilibrium unstressed density distribution of the rth chain atom about the first, whether the rth atom is a chain end or not, we obtain for the total (equilibrium unstressed) density distribution about an end of the chain:

$$ {}^{n}D_0(x, y, z) = \sum_{r=1}^{n} \frac{A}{r^{\frac{3}{2}}} \cdot \exp\left[-\frac{B}{r}(x^2+y^2+z^2)\right]. \quad (2) $$

This density distribution is spherically symmetrical and corresponds to the unstrained state. A linear high polymer which possesses configurational strain will have a different distribution among molecular shapes, and hence a different density distribution function which will not be spherically symmetrical, but rather ellipsoidally symmetrical, at least for small strains.

According to Wall,[5] a tensile stress S in the x direction changes the equilibrium distribution of chain end separations from the form (1) to a form which can be rewritten as follows (for small stresses):

$$ {}^{n}W_S(x, y, z) = \frac{A}{n^{\frac{3}{2}}} \cdot \exp\left\{-\frac{B}{n}\left[\frac{x^2}{(1+an)^2}+(1+an)(y^2+z^2)\right]\right\}, \quad (3) $$

where

$$ a = S/3\rho kT. $$

We now assume that in the presence of the stress the equilibrium distribution of the rth chain atom, whether it is a chain end or not, about the first, is given by the analogous expression (4). This specific assumption is admittedly not justified in any rigorous fashion, but is introduced as a reasonable first approximation. A rigorous justification may be possible.

$$ {}^{r}W_S(x, y, z) = \frac{A}{r^{\frac{3}{2}}} \cdot \exp\left\{-\frac{B}{r}\left[\frac{x^2}{(1+ar)^2}+(1+ar)(y^2+z^2)\right]\right\}. \quad (4) $$

It follows that the total equilibrium density distribution function in the stressed state, including the distribution of each successive chain atom about the first, is given by the equation:

$$ {}^{n}D_S(x, y, z) = \sum_{r=1}^{n} \frac{A}{r^{\frac{3}{2}}} \cdot \exp\left\{-\frac{B}{r}\left[\frac{x^2}{(1+ar)^2}+(1+ar)(y^2+z^2)\right]\right\}. \quad (5) $$

We now assume that the macroscopic strain is connected with the smeared-out molecular shape by the following equation:

$$ 1+\gamma_{xx} = \frac{L}{L_0} = \frac{\int_0^\infty\int_0^\infty\int_0^\infty x \cdot {}^{n}D_S(x, y, z)\,dx\,dy\,dz}{\int_0^\infty\int_0^\infty\int_0^\infty x \cdot {}^{n}D_0(x, y, z)\,dx\,dy\,dz}. \quad (6) $$

This compares the mean extension-in-x of a molecule in the strained state to that in the unstrained state. It is an extension of the ordinary kinetic theory approximation which compares the mean x separation of the chain ends with that in the unstrained state. (In the rest of the discussion, other subscripts will appear. In order to avoid multiple subscripts, it will be assumed that γ always refers to an x tensile strain, γ_{xx}.) Using the assumed density distribution (5) for the stressed state, it is possible to evaluate the integrals in (6) explicitly.

$$ 1+\gamma = \frac{\int_0^\infty\int_0^\infty\int_0^\infty x \cdot \sum_{r=1}^{n} \frac{A}{r^{\frac{3}{2}}} \cdot \exp\left\{-\frac{B}{r}\left[\frac{x^2}{(1+ar)^2}+(1+ar)(y^2+z^2)\right]\right\} dx\,dy\,dz}{\int_0^\infty\int_0^\infty\int_0^\infty x \cdot \sum_{r=1}^{n} \frac{A}{r^{\frac{3}{2}}} \cdot \exp\left\{-\frac{B}{r}[x^2+y^2+z^2]\right\} dx\,dy\,dz}, \quad (7) $$

[4] Cf. citations in reference 1–3.

[5] Cf. citations in reference 3.

$$1+\gamma=\frac{\sum_{r=1}^{n}(r^{\frac{1}{2}}+ar^{\frac{1}{2}})}{\sum_{r=1}^{n}r^{\frac{1}{2}}}. \tag{8}$$

As an approximation we replace these two sums by integrals.

$$1+\gamma=\frac{\int_1^n(r^{\frac{1}{2}}+ar^{\frac{1}{2}})dr}{\int_1^n r^{\frac{1}{2}}dr}, \tag{9}$$

$$1+\gamma=1+\frac{3a}{5}\cdot\frac{(n^{5/2}-1)}{(n^{\frac{3}{2}}-1)}. \tag{10}$$

For large n, this reduces to:

$$1+\gamma=1+\frac{3a}{5}\cdot n=1+\frac{nS}{5\rho kT}, \tag{11}$$

$$\gamma=\frac{nS}{5\rho kT}. \tag{12}$$

Except for the numerical factor, this result agrees with that obtained by the ordinary kinetic theory, where only the distribution of chain ends is considered. Considering only the ends, we would have obtained:

$$1+\gamma=\frac{\int_0^\infty\int_0^\infty\int_0^\infty x\cdot\exp\left\{-\frac{B}{n}\left[\frac{x^2}{(1+an)^2}+(1+an)(y^2+z^2)\right]\right\}dxdydz}{\int_0^\infty\int_0^\infty\int_0^\infty x\cdot\exp\left\{-\frac{B}{n}(x^2+y^2+z^2)\right\}dxdydz}, \tag{13}$$

$$1+\gamma=1+\frac{nS}{3\rho kT}, \tag{14}$$

$$\gamma=\frac{nS}{3\rho kT}. \tag{15}$$

The extended analysis thus yields no significantly new information concerning the equilibrium value of the *total* configurational elastic strain. The value of the new treatment lies in the fact that we can now resolve the total configurational strain into a series of terms $\gamma_1, \gamma_2, \gamma_3, \cdots$, which indicate the strain contributions of chain sections of different lengths. This analysis follows.

First, for illustration, we will divide γ into a part γ_1 which is due to the uncurling and orientation of chain segments which are shorter than the length m, and a part γ_2 which is due to the uncurling and orientation of longer chain segments.

Consider the various segments, containing m chain atoms, as though they were complete molecules. There will be a certain density distribution ${}^mD(x, y, z)$ which will represent the average, or smeared-out, extension in space of these segments, in exactly the fashion that ${}^nD(x, y, z)$ represents the whole molecule.

$${}^mD_S(x, y, z)=\sum_{r=1}^{m}\frac{A}{r^{\frac{1}{2}}}\times\exp\left\{-\frac{B}{r}\left[\frac{x^2}{(1+ar)^2}+(1+ar)(y^2+z^2)\right]\right\}. \tag{16}$$

The elastic strain which results from the uncurling and orientation of short segments (containing less than m atoms) may be designated by γ_1, and the strain which results from the uncurling and orientation of long segments by γ_2.

$$\gamma_1=\frac{\iiint x^mD_S(x, y, z)dxdydz}{\iiint x^mD_0(x, y, z)dxdydz}-1, \tag{17}$$

$$\gamma_2=\frac{\iiint x^nD_S(x, y, z)dxdydz}{\iiint x^nD_0(x, y, z)dxdydz}-\frac{\iiint x^mD_S(x, y, z)dxdydz}{\iiint x^mD_0(x, y, z)dxdydz}, \tag{18}$$

$$\gamma=\gamma_1+\gamma_2$$

$$=\frac{\int\int\int x^n D_S(x, y, z)dxdydz}{\int\int\int x^n D_0(x, y, z)dxdydz}-1. \quad (19)$$

By a generalization of this procedure, the total strain γ can be resolved into $(n-1)$ components, $\gamma_2, \gamma_3, \gamma_4 \cdots \gamma_n$, where each contribution arises from the shape changes of molecular segments of a given size.

$$\gamma_j=\frac{\int\int\int x^i D_S(x, y, z)dxdydz}{\int\int\int x^i D_0(x, y, z)dxdydz}$$

$$-\frac{\int\int\int x^{i-1} D_S(x, y, z)dxdydz}{\int\int\int x^{i-1} D_0(x, y, z)dxdydz}, \quad (20)$$

$$\gamma=\sum_{j=2}^{n}\gamma_j. \quad (21)$$

The form of the above equations suggests a new set of coordinates $(X_1, Y_1, Z_1, X_2, Y_2, Z_2, \cdots X_n, Y_n, Z_n)$ to describe the configuration of a single molecule and thus take the place of the atomic Cartesian coordinates $(x_1, y_1, z_1, x_2, y_2, z_2, \cdots x_n, y_n, z_n)$. Let X_1, Y_1, and Z_1 represent the x, y, and z coordinates, respectively, of the center of gravity of the polymer molecule. Let X_j be defined by the expression:

$$X_j=M_j-M_{j-1}, \quad (22)$$

where $M_j=\dfrac{\bar{L}_j}{\int\int\int x\cdot {}^iD_0(x, y, z)dxdydz}$,

where $\bar{L}_j$ = the average value of L_j for all segments of size j in the molecule under consideration, where L_j for a segment of size j is given by:

$$L_j=\tfrac{1}{8}\sum_{k=2}^{j}|x_k|,$$

and x_k is the x displacement of the kth chain atom of a given segment from the first atom of that segment. Thus just as γ_j represents the macroscopic x tensile strain due to the uncurling and orientation of molecular chain segments containing j atoms when a given distribution of shapes is present, so X_j represents the mean relative uncurling and x orientation of the chain segments containing j atoms in a single polymer molecule of a definite shape.

If the new coordinates X_i, Y_i, etc., were a linear combination of the atomic Cartesian coordinates, $x_1, y_1, z_1, x_2, y_2, z_2, \cdots$ etc., then they would represent an equivalent set of independent variables which together would define the configuration of a polymer molecule. Actually, the *absolute magnitudes* of certain quantities enter in place of the algebraic values. Hence the new "coordinates," $X_1, X_2, \cdots$, do not represent a linear transformation of the original Cartesian coordinates. The X's are not strictly a set of "normal coordinates" for the polymer molecule, although they are introduced for analogous reasons.

Just as a given distribution of molecular configurations results in a series of density distributions ${}^iD(x, y, z)$, so it also results in a series of probability distributions governing the various X's—e.g., $D(X_j)$. The strain γ_j is given by:

$$\bar{X}_j=\gamma_j=\int_{-\infty}^{\infty}X_j D(X_j)dX_j. \quad (23)$$

In particular, the equilibrium unstressed distribution of molecular shapes, which gave rise to the density distributions ${}^mD_0(x, y, z)$, will also give rise to the distributions $D_0(X_j)$, such that

$$\gamma_j=\bar{X}_j=\int_{-\infty}^{\infty}X_j D_0(X_j)dX_j=0. \quad (24)$$

In the presence of a stress, there will be a new equilibrium distribution of molecular shapes, and hence a new equilibrium distribution of the values of each of the X's, and new equilibrium values of the macroscopic strain contributions $\gamma_2, \gamma_3, \gamma_4, \cdots \gamma_n$. The local kinkiness, defined by the X's of low index, will take on its equilibrium distribution rather quickly; the long range convolutions, defined by the X's of large index, will assume the new equilibrium distribution more slowly.

It follows from Eqs. (5) and (20) that the equilibrium value of γ_i is given by:

$$\gamma_i=S/5\rho kT. \quad (25)$$

Similarly, the equilibrium value of $\bar{X}_j$, the mean value of the coordinate X_j, has the value $S/5\rho kT$.

Finally, the contribution to the elastic compliance in tension which is furnished by the configurational changes of segments containing n atoms (in the range dn) is given by:

$$J(n)dn=(1/5\rho kT)dn. \tag{26}$$

We can now return to the question of the rate of attainment of elastic equilibrium. We have advanced the general hypothesis that the local kinkiness, defined by the X's of low index, will take on its equilibrium distribution rather quickly, while the long range convolutions of the chains, defined by X's of large index, will assume the new equilibrium distribution more slowly. Let us now specifically assume that each contribution to γ relaxes into its new equilibrium value in a simple exponential fashion, with a retardation time τ which is connected with the chain length of the corresponding segment in the same fashion that the melt viscosity of a linear polymer is connected with the molecular chain length:[6]

$$\tau_n=Ae^{b\sqrt{n}}e^{\Delta E/RT}. \tag{27}$$

This would seem to be a reasonable assumption as long as n is considerably greater than the length of the effective segments which act in flow and diffusion.

If we combine Eq. (27), which gives the retardation time for the configurational changes of a chain section of size n, with Eq. (26), which gives the elastic compliance associated with a range of sizes dn, we can deduce the function $J(\tau)$, which gives the elastic compliance as a function of retardation time. The function so obtained is:

$$\begin{aligned} &=0 \quad \text{for} \quad \ln\tau<\alpha \\ J(\tau)d\tau&=\frac{2}{5b^2\rho kT} \\ &\cdot\left(\frac{\ln\tau-\ln A-\Delta E/RT}{\tau}\right)d\tau \qquad (28) \\ &\qquad \text{for} \quad \alpha<\ln\tau<\beta \\ &=0 \quad \text{for} \quad \ln\tau>\beta \end{aligned}$$

where

$$\alpha=\ln A+\frac{\Delta E}{RT}, \quad \beta=\ln A+\frac{\Delta E}{RT}+b\sqrt{n}.$$

In the above form, the dependence on temperature as well as on τ is given. At a definite temperature, the above equation can be expressed in the form:

$$J(\tau)d\tau=\frac{C\ln\tau-D}{\tau}d\tau \quad \text{for} \quad \alpha>\ln\tau>\beta. \tag{29}$$

The theory thus leads to precisely the sort of mechanical behavior which has been empirically assigned to amorphous polymers—i.e., a distribution of elastic compliance over a wide range of retardation times. The theory as presented here must certainly fall down very badly in the low τ region, which corresponds to the shape changes of very short segments. In the first place, the equilibrium distribution law (1) should not be applied to very short sections. Furthermore, the assumption that τ_n is given by Eq. (27) cannot be expected to hold for segments which are not several times as long as the "Eyring segments" which serve as the moving units of flow and diffusion. All assumptions involved in the theory are much more justified in the high τ region of the spectrum. In the case of very high molecular weight polymers, this high τ part of the spectrum should be relatively more important than in the case of a low molecular weight polymer, and hence the theory should be relatively more satisfactory for a very high polymer than for a low polymer.

In spite of the fact that the present treatment introduces specific assumptions which, at best, should be applied only to large segments, the writer feels that the general method involved represents a rational approach to the molecular theory of viscoelastic behavior in linear amorphous polymers. The theory can presumably be improved in the low τ region by the following extensions:

(1) Equation (1) is rigorously applicable only to chain atoms which are separated by a large number of chain units. A return should, therefore, be made to the original stochastic problem from which (1) is derived as a limiting form. A new distribution function $W(x, y, z, n)$, valid for small n as well as large, should replace (1) in the present treatment.

(2) An improved approximation to the function $\tau(n)$ should be developed to replace (27). An heuristic approach would seem indicated here. For example, the retardation times for shape changes of small segments might be expected to depend upon segment length in a manner analogous to that in which the viscosities of short molecules depend upon their length.

[6] P. J. Flory, J. Am. Chem. Soc. **62**, 1057 (1940).

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Molecular Constants and Chemical Theories

III. Bond Moments of Higher Valence States

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In continuation of Part I and Part II of this paper, bond moments are calculated for such molecules as are formed by a marked central atom in a higher state of valency. Again the classical structures are taken as a basis. The bond moments are additive in the same molecule and unchanged from molecule to molecule as long as the multiplicity of the bond and the state of valency of either atom remain the same. This treatment on the basis of classical formulae makes possible the simple and straightforward calculation of the total moments of a considerable number of molecules formed by pentavalent nitrogen (azoxybenzenes, *N*-ethers of nitrobenzophenoneoximes), for which no other such calculation has been possible so far. Observable facts of dipole measurements, therefore, are at least as well represented by the classical structures and their underlying concepts, as by any other theory of the covalent bond. Hence, dipole moments do not provide any evidence of the existence of such linkages as a semipolar double bond or its wave-mechanical equivalent, i.e., enhanced resonance with ionic parent structures.

INTRODUCTION

IT has been shown[1] that additive molecular constants are unable to distinguish between different types of covalent linkage. In this paper a more complete system of bond moments will be developed. It will be seen that the electric moments of molecules may be separated into bond moments, which remain strictly additive as long as the atoms retain their state of valency. The classical structures are taken as the basis of calculation, their validity having been discussed previously.[1] It follows that dipole moments do not provide any criterion which could distinguish between these classical structures and others which use the concept of the coordinate (semipolar) link or enhanced resonance with ionic parent structures. Again this refers not to molecules with aromatic structures but to those of Werner's first order which are formed by a marked central atom. It has been shown that for them the energy difference between different resonance forms is very great, if compared with their bond energies.

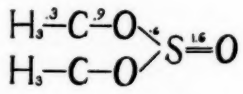
The new bond moments depict the course of polarity in the periodic table in a very reasonable way, and permit the drawing of some conclusions on the change of polarity in the transition of an atom from one valence state to another. Furthermore, these bond moments are then applied to a considerable number of molecules, whose total moments have up to now remained unexplained. Typical are the azoxybenzenes and certain oximes, formed by imino-nitrogen. All attempts to account for these moments on the basis of constant bond moments of tetracovalent nitrogen have failed, but the new bond moments ascribed to pentacovalent nitrogen permit their reconstruction with the same ease as those of any other molecule.

CALCULATIONS OF BOND MOMENTS

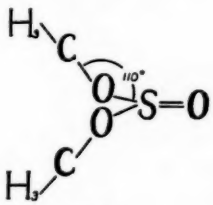
According to the underlying concepts of the classical structures, it has to be assumed that the polarity of a certain bond changes with the valency of the central atom. The moment of the S—Cl bond, for instance, cannot be the same in SCl_2, $SOCl_2$, and SO_2Cl_2, as the field of the core of S^{6+} is screened by two *s* and two *p* electrons in SCl_2, by two *s* electrons in $SOCl_2$, and by none in SO_2Cl_2. It is, therefore, not possible to establish the value of $\mu(S{=}O)$ in $S^{IV}OCl_2$ by subtracting $\mu(S^{II}Cl_2)$ from $\mu(S^{IV}OCl_2)$. In such calculations naturally a great variety of quite irregular values for the S=O bond is obtained. Following the other course, it is expected to obtain three values each for the S—Cl and the S=O bond, each of them definitely associated with one of the three valence states of sulphur, and constant in any molecule formed by this atom in this particular valency.

[1] R. Samuel, J. Chem. Phys. **12**, 167, 180 (1944).

From the purely arithmetical point of view, this concept immediately increases the number of unknowns. In some cases, like tetravalent sulphur, sufficient moments have been measured to permit an unambiguous solution of all equations. In others, e.g., tetravalent selenium, this is not so, and an additional equation has to be supplied by extrapolation. In this instance, it is assumed that the ratio of $\mu(Se^{IV}{=}O):\mu(Se^{IV}{-}Cl)$ is the same as that of $\mu(S^{IV}{=}O):\mu(S^{IV}{-}Cl)$. It will be seen that some care has been taken to reduce such extrapolations to a minimum and to compare the unknown strength of a bond only with another one of very similar nature. The electric moments of a number of more complex molecules are then calculated and agree with the observed value. As each calculation represents an independent equation these extrapolations may be taken as justified. It should be borne in mind that bond moments cannot be expected to behave rigorously additively, on account of the effects of the solvent and of the induction of one moment upon another. The table of bond moments by necessity comprises only rough values, which, however, are entirely sufficient to throw some light upon the nature of polarity, when related to the position of the atom in the periodic table. But, for this reason small errors introduced by such an extrapolation do not matter much, as is also the case with small variations of valence angles. The moments calculated by Smyth[2] are again taken as a starting point, particularly for molecules formed by atoms in their lowest valence state.*



(1a)
μ(calculated) = 2.8,
μ(observed) = 2.9.



(1b)
μ(calculated) = 1.8.

[2] C. P. Smyth, J. Am. Chem. Soc. **60**, 183 (1938) and earlier.

* All moments not otherwise mentioned are taken from the compilation in Trans. Faraday Soc. **30** (1934) or the article of E. Bergmann and A. Weizmann, Chem. Rev. **29**, 553 (1941). In addition, C. P. Smyth, G. L. Lewis, A. J. Grossman, and F. B. Jennings, III, J. Am. Chem. Soc. **62**, 1219 (1940); I. E. Coop and L. E. Sutton, Trans. Faraday Soc. **35**, 505 (1939). Electron diffraction data from L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936).

As most of the moments are measured in solution, these values have been taken as a basis rather than the slightly different ones for the gaseous state. Although these represent the true values, too few are known to make an extensive comparison possible at this time.

BOND MOMENTS OF TETRAVALENT SULPHUR, SELENIUM, AND TELLURIUM

For sulphur dioxide the moment is 1.61D and the valence angle has been determined[3] as 121°±5°; the moment of $S^{IV}{=}O$, therefore, is 1.6D. For $SOCl_2$ ($\mu = 1.44$) the angle (ClSCl) is 114°, that of (OSCl) = 106°±1.[4] This gives an angle of about 120° for the S=O bond against the bisecting line of the angle (ClSCl), and with the above value of $\mu(S^{IV}{=}O)$, $\mu(S^{IV}{-}Cl)$ is calculated to be 1.1.

In exactly the same way but assuming the ratio of $\mu(Se^{IV}{=}O):\mu(Se^{IV}{-}Cl)$ to be the same as that of $\mu(S^{IV}{=}O):\mu(S^{IV}{-}Cl)$ we obtain from $SeOCl_2$ ($\mu = 2.6$) the values of $\mu(Se^{IV}{=}O) = 2.1$ and $\mu(Se^{IV}{-}Cl) = 1.4$. The angle (Cl Se Cl) is taken as 110°, that of its bisector against Se=O as 115°. Both are slightly smaller than the corresponding angles in $SOCl_2$, because the longer distances should reduce the repulsive forces.

In order to justify these values and to show their additivity, they may be applied to some other molecules. Dimethyl sulphite may serve as a first example. The value of the $(S^{IV}{-}O)$ single bond may be obtained by extrapolation. Assuming the ratio $\mu(S^{IV}{-}O):\mu(S^{IV}{-}Cl)$ to be the same as that of $\mu(C^{IV}{-}O):\mu(C^{IV}{-}Cl)$, a value of 0.6D obtains, while $\mu(S^{IV}{-}O):\mu(S^{IV}{=}O) = \mu(C^{IV}{-}O):\mu(C^{IV}{=}O)$ results in the value of 0.5D.

As the sulphite ion exhibits tetrahedral angles, we take 110° for the angle (O—S—O) and 125° for its bisecting line against S=O, and again 110° for (COS). Then with the above values of the individual moments that of the molecule is calculated to be 2.8 in position (1a), the observed value in 2.9. A rotation of the H—C—O moment by 180° about the S—O axis would reduce the moment to 1.8, showing position (1a) as the preferred one. The same valence angles as in diphenyl sulphite

[3] V. Schomaker and D. P. Stevenson, cf. L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1944).

[4] K. J. Palmer, J. Am. Chem. Soc. **60**, 2360 (1939).

should persist in diphenyl sulphoxide as the resolution into optically active isomeric forms of very similar compounds shows the S^{IV} atom on the apex of a pyramidal structure. The dipole moment of Ph_2SO of 4.1D then permits us to calculate the moment of the carbon-sulphur bond. The moment of *p*, *p'*-dichloro diphenyl sulphoxide of 2.7 is much too small to be explained by a slight change of valence angles. The difference of these two moments is of the correct order for $\mu(H\rightarrow C)-\mu(C\rightarrow Cl)$. Hence, in the sulphoxides the bond moment $S^{IV}\leftarrow C$ is pointing towards the sulphur atom. The direction can immediately be verified, but is nevertheless unexpected. Its implication will be discussed below.

With $\mu(S^{IV}\rightarrow O)=1.6$, and with angles of 110° and 125°, the moment $\mu(S^{IV}\leftarrow Ph)$ in diphenyl sulphoxide comes to 2.6D, leaving about 2.2D for $\mu(S^{IV}\leftarrow C_{AR})$. For the aliphatic carbon atom the slightly smaller value of 2.1D is derived from diisobutyl sulphoxide ($\mu=3.9$). The value of 2.2, now used for the substituted molecules, leads to

p-chloro diphenyl sulphoxide:

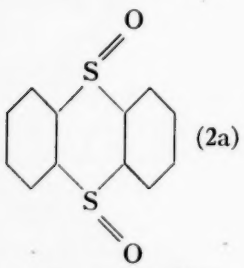
μ(calculated) = 3.3, μ(observed) = 3.9,

p, *p'*-dichloro diphenyl sulphoxide:

μ(calculated) = 2.4, μ(observed) = 2.7.

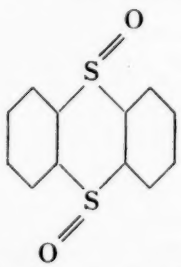
The slight difference between calculated and observed values may be due to induction. It will be seen that such discrepancies are particularly persistent for halogen substituted phenyl groups.

These bond moments may now be applied to the two isomers of thianthrene sulphoxide, the moments of which have been measured by Bergmann and Tschudnowsky[5] as $\mu=1.7$ and $\mu=4.2$ for the two forms with melting points of 279° and 246°, respectively. Like thianthrene



(2a)

$\mu=1.7$, m.p. = 279°,
μ(calculated) = 1.7.



(2b)

$\mu=4.2$, m.p. = 246°,
μ(calculated) = 4.1.

[5] E. Bergmann and M. Tschudnowsky, Ber. d. D. Chem. Ges. **65**, 467 (1932).

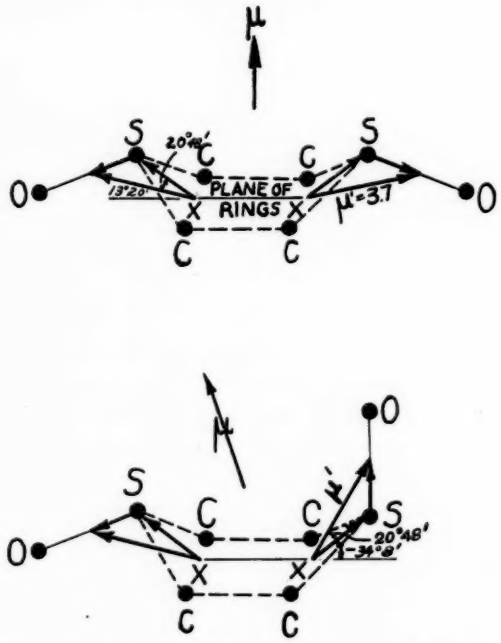


FIG. 1. Cross section of the two forms of thianthrene sulphoxide in the (O−S − − −S−O) plane. Broken lines refer to planes normal to that of the paper. The internuclear distances are drawn to scale, i.e., (S=O) = 1.4A, ($X-X$) = ($C_{AR}-C_{AR}$) = 1.4A. (S−X) = 1.03A follows from (S−C) = 1.8A. The scale of the moment vector (arrows) is independent of that of the distances and chosen to make the S−X vector as long as the S−X distance. All angles follow from simple geometrical calculations under the one assumption that the valence angle (CSC) is 110°.

itself, they cannot be planar if the valence angle (CSC) be maintained at 110°. The S—C bonds are 1.8A and the projection of S in the plane of the rings must form an angle of 120° with the two neighboring C atoms. Then the (CSC) plane forms with that of the rings an angle of 34° 8′ and this is, therefore, also its angle with the bisector of the angle (CSC). On the other hand, as the four (C—H) moments cancel out, we have only to consider the moments ($S^{IV}\leftarrow C$). With the valence angle of 110° at S, they form a resultant of 2.5D. The ($S^{IV}\rightarrow O$) moment of 1.6 added under an angle of 125° produces a total moment of each (OSC_2) structure of 3.7D, and this vector forms an angle of 20° 48′ with the bisector of (CSC). Its angle against the plane of the rings (Fig. 1) is 34° 8′ − 20° 48′ = 13° 20′. The vector sum of two such moments, which now meet under an angle of (180° − 2×13° 20′ =)153° 20′, is 1.7D, exactly as observed for form (2a). Rotating one S=O bond by 180° into the other possible position makes the

angle between the two 3.7 vectors $153° 20' - 2 \times 20° 48' = 111° 44'$. The vector sum of these two is then 4.1, while 4.2 has been observed for form (2b). Because the shift of the ($S^{IV} \rightarrow O$) vector affects only the direction of the two weaker ones of the four composing moments and as they do not compensate, thianthrene sulphoxide provides an exceptional case, in which the *cis*-form (2a) exhibits a weaker moment then the *trans*-form (2b) and the lower melting point of the *trans*-form, therefore, is associated with the higher moment. The easy representation appears to confirm the numerical values and the directions of the two moments ($S^{IV} \rightarrow O$) and ($C \rightarrow S^{IV}$), and also the contention that a moment like the former, originally taken from SO_2, remains constant and additive as long as sulphur is tetravalent.

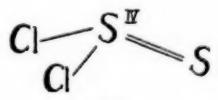
Next we turn to the molecules S_2Cl_2 and Se_2Cl_2. The results of electron diffraction measurements on sulphur monochloride[4] have been interpreted as indicating an extended structure Cl—S—S—Cl. However, the absorption spectra[6] of the vapors clearly indicate the existence of a double bond S=S in this molecule and of a Se=Se bond in both selenium monochloride and selenium monobromide. To the present writer the very careful investigation of the Raman effect[7] of $SOCl_2$ and S_2Cl_2 appears to be decisive, which goes to show that both molecules possess the same branched structure. On account of the larger distances the repulsive forces again should be slightly reduced as compared with $SOCl_2$. For S_2Cl_2 we assume the same value of 114° for the angle (ClSCl), but the slightly reduced value of 115° for its bisecting line against S=S. For Se_2Cl_2 both angles are taken as 110°. Slight changes would hardly affect the results. The bond moment of $S^{IV}=S^{II}$ will have the same ratio against $S^{IV}=O$ as for instance $C^{IV}—S$ against $C^{IV}—O$, and $\mu(S^{IV}=S) = 0.94\mu(S^{IV}=O)$ is taken as 1.5D.* Extrapolation by means of $\mu(Se^{IV}=Se) : \mu(Se^{IV}=O) = \mu(S^{IV}=S) : \mu(S^{IV}=O) = 0.94$ gives $(Se^{IV}=Se^{II}) = 2.0$.

[6] R. K. Asundi and R. Samuel, Proc. Phys. Soc. London **48**, 28 (1935); S. L. Hussain and R. Samuel, *ibid.* **49**, 679 (1937); cf. M. Jan-Khan and R. Samuel, *ibid.* **48**, 626 (1936).

[7] F. Matossi and H. Aderhold, Zeits. f. Physik **68**, 683 (1931).

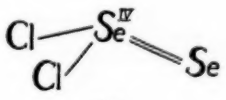
* The value of $\mu(C^{IV}-S^{II}) = 0.74$ has been used which follows from that of $(C_2H_5)_2S$, $\mu = 1.58$, if the correct value of 92° is employed for the valence angle.

Using these values together with those derived for S^{IV}—Cl and Se^{IV}—Cl in the oxychlorides, we obtain:



(3)

μ(calculated) = 1.5,
μ(observed) = 1.6.



(4)

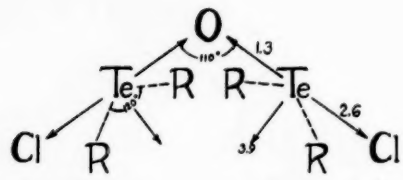
μ(calculated) = 2.1,
μ(observed) = 2.1.

Finally, the moments of molecules of the type $Ph_2Se\,Cl_2$ have been measured recently[8] and may now be considered. Pauling[9] suggests for them the structure of a trigonal bipyramid, in which the "lone pair" of tetravalent sulphur or selenium occupies one of the equatorial positions. Although in the present view the *d* electrons are needed for the formation of a bond only in a higher approximation,[1] this appears to be the most plausible structure. It follows that the two moments directed towards the apices compensate, and the other two will form an angle of approximately 120°. If the phenyl groups take up the apical positions the moments of Se^{IV} and Te^{IV} against C cannot be determined. However, a survey of the moments shows that in all likelihood this cannot be so. For $Ph_2Se\,Cl_2$ and $Ph_2Se\,Br_2$, for instance, the moments are observed as 3.2 and 3.4D. Their difference is too small and their absolute value much too high for such a structure, but both agree with one in which the halogens are at the apex and the radicals in the equatorial position. The small difference between them is then due to solvation or to the (X Se X) angle being slightly less then 180°, and the small resultant then opposes that of the (Ph Se Ph) structure. As the angle of the latter is supposed to be 120°, the total moment of the molecule is identical with that of the bond against the phenyl radical, and we obtain immediately the following values:

$Ph_2Se\,Br_2 = 3.4$, $(Se^{IV} \rightarrow Ph) = 3.4$,
$(Se^{IV} \rightarrow C_{AR}) = 3.8$,
$(p-Me\,C_6H_4)\,Te\,Br_2 = 3.2$, $(Te^{IV} \rightarrow R) = 3.2$,
$(Te^{IV} \rightarrow C_{AR}) = 3.9$,
$Te\,Cl_4 = 2.6$, $(Te^{IV} \rightarrow Cl) = 2.6$.

[8] K. A. Jensen, Zeits. f. anorg. allgem. Chemie **250**, 245, 257, 268 (1943).

[9] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1944), second edition.



(5)*

μ(observed) = 6.1. μ(calculated) = 5.8.

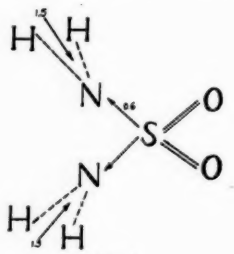
The molecule $[(p\text{—Me—}C_6H_4)_2\,Te\,Cl]_2O$ may be used to verify these structures and values. The two reduced bipyramids have a common apex at the O atom (5)* and the two Cl—Te—O axes enclose the valence angle of oxygen of about 110°. The two Te—tolyl bonds at each Te atom, each possessing approximately $\mu = 3.9$, form a resultant each of the same value 3.9. These resultants, both normal to (O—Te—Cl), enclose an angle of 110° and their vector sum is 4.3. The two Te—Cl moments (also 110°) produce a resultant of 3.0 in the same direction. The Te—O bonds (according to the conditions found in dimethyl sulphite) will possess a moment of about half that of Te^{IV}—Cl or about 1.3. Their resultant is 1.5, pointing in the opposite direction. Hence, we obtain for the total moment of the molecule $4.3+3.0-1.5=5.8$D, the observed value is 6.1D. Considering the scarcity of data and necessity of extrapolations, the agreement is very good indeed. It shows again the bond moments to be constant from molecule to molecule. Incidentally it also shows that the (Se^{IV}—C) and (Te^{IV}—C) moments point in the direction of the carbon atom. As to diphenyl selenoxide, the individual bond moments now being established, it is concluded from the moment $\mu(Ph_2\,Se\,O) = 4.4$, that the angle (Ph Se Ph) probably lies between 95° and 110°, that of its bisector against Se=O between 110° and 120°. However, these geometrical structures are not always the most stable ones. Among these molecules and even more so among those formed by the pentavalent atoms (discussed below) which form similar bipyramids, complete changes appear to occur frequently. Thus, the high value of $\mu = 4.4$ appears to indicate that in dibenzyl sulphide diiodide $(C_7H_7)_2SI_2$ the lone pair takes the place on the apex. The moment calculated for such a structure (with $\mu(S^{IV}\text{—I}) = 1.1$) comes to 4.0D.

* The broken lines refer to a plane normal to that of the paper.

BOND MOMENTS OF HEXAVALENT SULPHUR

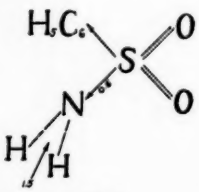
The natural starting point for molecules formed by hexavalent sulphur is sulphuryl chloride, $\mu(SO_2Cl_2) = 1.8$. Its structure is almost exactly that of the regular tetrahedron,[10] and as the sulphate ion also possesses tetrahedral structure, this structure is assumed for such molecules in general. Using again the ratio $\mu(S^{VI}\text{—Cl}) : \mu(S^{VI}\text{=O}) = 3:5$ the moments $\mu(S^{VI}\text{—Cl}) = 2.4$ and $\mu(S^{VI}\text{=O}) = 3.9$ are obtained. From diethyl sulphone a value of 0.4 can then be calculated for $\mu(S^{VI}\rightarrow C)$. It is, however, doubtful whether heavier organic sulphones possess the same geometric structure, and at this time it is sufficient to know that the moment of this bond contributes a small positive amount.

If we estimate the moment of $S^{VI}\text{—}N^{III}$ by means of the ratio $\mu(C^{IV}\rightarrow Cl) : \mu(C^{IV}\rightarrow N) = \mu(S^{VI}\rightarrow Cl) : \mu(S^{VI}\rightarrow N^{III}) = 3.5$, the sulphone amide permits us to verify the values for both S^{VI}=O and S^{VI}—Cl simultaneously. For $S^{VI}\rightarrow N$, 0.6D results, and for the amide, according to formula (6a) and the ammonia angles, the moment is 3.9, precisely the observed value. Rotation of the $N\leftarrow H_2$ moment by 180° about the S—N axis (6b) would lead to 2.2D, and the position of (6a) is the preferred one. For benzene

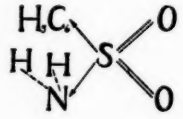


(6a)
μ(calculated) = 3.9,
μ(observed = 3.9).

(6b)
μ(calculated) = 2.2.



(7a)
μ(calculated) = 2.9.



(7b)
μ(calculated) = 5.1,
μ(observed) = 5.09.

[10] K. J. Palmer, J. Am. Chem. Soc. **60**, 2360 (1938).

sulphone amide,[11] the observed value obtains for form (7b). For both molecules the influence of free rotation appears to be negligible. The two prevailing forms are characterized by the repulsion of the hydrogen atoms in sulphonamide, and attraction of the hydrogens to the phenyl ring in benzene sulphonamide. The reason probably is the positive charges at the hydrogen atoms and the negative charges at the ring.

BOND MOMENT OF PENTAVALENT PHOSPHORUS

Not much is known about the electric moments of molecules formed by the atoms of the fifth family in their state of maximal valency. $Ph_3 As Cl_2$, $Ph_3 Sb Cl_2$, $Ph_3 Bi Cl_2$ possess no definite dipole moments[8] and, probably, form trigonal bipyramids with the chlorine atoms at the apices. The structure of $POCl_3$ and $PSCl_3$ approaches that of the regular tetrahedron.[12] But the moments of $Ph_3 PO$, $Ph_3 PS$, and $Ph_3 PSe$ (4.3, 4.7, 4.8, respectively) cannot be explained on such a basis. Their difference appears to be too small and their increase in the wrong direction for the PO (S, Se) moment to oppose the vector sum of the others. Such moments as $Ph_3 As \cdot (OH) \cdot Cl$ ($\mu = 9.2$) and $Ph_3 Sb \cdot (OH) \cdot Cl$ ($\mu = 3.0$) appear to be incompatible for the same geometric structure. Apparently the chlorine atom and the phenyl radical exchange their position frequently. $SbCl_5$ possesses a moment in some solvents, but not in others. A more detailed analysis (including that of amine oxide, mentioned earlier[1]) appears premature.

Hence, we confine ourselves to calculating $\mu(P^V{=}O) = 6.2$ and $\mu(P^V{-}Cl) = 3.7$ from $\mu(POCl_3) = 2.4$, assuming again the ratio of 5:3 between them. Thus, again extrapolating $\mu(P^V{=}S)$ as slightly less then $0.9 \times \mu(P^V{=}O)$, we take it as 5.4D and calculate the moment of $(PSCl_3)$ to be $5.4 - 3.7 = 1.7$, while the observed value is 1.4D. The moment $(P^V \rightarrow Ph)$ probably will lie between 1.5 and 2D, pointing towards Ph.

BOND MOMENTS OF PENTAVALENT NITROGEN

In the following molecules nitrogen is taken as pentacovalent according to the classical structures. It has been shown previously[1] that neither band spectra nor wave-mechanical treatment provides a basis for the hypothesis of a covalency maximum of four of this atom. London's early remark[13] about the uncoupling of p electrons concerns only the isolated atom but not the molecule, as already in the diatomic molecule twice the number of p orbitals are available for this process. While in the oxygen atom two of the four p electrons are paired, they become uncoupled in the oxygen molecule as shown by its paramagnetic ground level $^3\Sigma$. If we indicate those electrons which are uncoupled and available for molecular formation by lines, and by dots those which are paired in the atom or by sharing, the electronic formula is $>O : : O :$ (with two dots under each O).

If now one of these free p electrons is removed by ionization, the electron configuration of O_2^+ and, therefore, of NO obtains, which is that of the nitroso stage, i.e.,

$$-\overset{\oplus}{O} : : O : \quad \text{and} \quad -N : : O :$$

If, however, one of the s electrons is removed, an excited O_2^+ or NO is produced (formed by O or N in sp^4), with three free valencies,

$$>\overset{\oplus}{O} : : O : \quad \text{and} \quad >N : : O :$$

Two of these three electrons are those originally unpaired in the ground level of O_2, the third loses its partner through ionization. Hence, as both wave-mechanical treatments satisfactorily account for the paramagnetic ground level of O_2, they also automatically both establish and prove the existence of a nitrogen atom with five electrons capable of linking other atoms. The full number of five is developed from the stage of the diatomic molecule onwards. The bonding character of these electrons in the theory of molecular orbitals has been discussed previously;[1] in the electron-pair bond theory this question does not arise. A comparison of the configurations of O_2 and excited NO with those of O_2^+ and unexcited NO and with those of O_2^{2+}, NO^+, and CO will show that the unpaired electrons of excited NO are those of the N atom.

[11] W. D. Kumler and I. F. Halberstadt, J. Am. Chem. Soc. **63**, 2182 (1941).

[12] L. O. Brookway and J. Y. Beach, J. Am. Chem. Soc. **60**, 1836 (1938); J. Y. Beach and D. P. Stevenson, J. Chem. Phys. **6**, 75 (1938).

[13] F. London, Zeits. f. Physik **46**, 455 (1938).

Some bond moments of pentavalent nitrogen have been considered in Part II of this series.[1] The calculations were based on Smyth's value of 3.3D for the $N^{V}{=}O$ bond in the nitro group.[2] This figure, however, is derived under the assumption that the C—N bond of the group points against nitrogen and is in fact the same as the $C—N^{III}$ bond, e.g., of the amines. However, the basic concept of a change of polarity with change of valency has to be applied uniformally here as elsewhere, and the $C—N^{III}$ and the $C—N^{V}$ bond cannot be considered as identical. The moment of $C{=}N^{V}$ shows that the $C—N^{V}$ single bond too will be directed against the carbon atom, and although the figures involved are not high, this makes necessary a recalculation of the moments of bonds involving pentavalent nitrogen. The essential features of Part II (Section 3) remain unchanged, as there only linear molecules with two opposing moments have been considered.

For the nitro group a number of experimental values have been observed, which vary from 3.2 and 3.8D of nitro methane in solution and the gaseous phase, respectively, to 3.9 and 4.2D of nitrobenzene in the same conditions. For the nitro group proper this leads to values between 3.4 and 4.5D. If we take a mean value of 4.0 as the basis of calculation, we derive by the same process as previously[1] the following bond moments, the N^{V} atom always being the positive partner:

$N^{V}{=}O$ 4.4, $N^{V}{\equiv}N^{III}$ 4.2, $N^{V}{=}C$ 2.6,
$N^{V}—O$ 1.4, $N^{V}{=}N^{III}$ 2.8, $N^{V}—C$ ~1.0.

These values may now be verified by calculating the moments of a great number of molecules. Some of them are given here, and for this purpose particularly those have been selected for which up till now no calculation has been possible at all. The valence angle ($C{=}N^{V}—O$) has been taken as that of ($O{=}N^{V}—O$), i.e., 127°. For the angle ($Ph—N^{III}—N^{V}$) of the azoxybenzene and its derivatives that of 120° has been used as observed between a single and a double bond at N^{III} in the azides. A small change would not affect the results appreciably.* For $\mu(N^{III}—Ph)$ Sutton's value[14] of 1.3D has been adopted, leading to about 0.9 for $\mu(N^{III}—C_{AR})$.

Methyl Nitrate:

$H_3C—O—NO_2$ $\quad$ $H{\rightarrow}C{\rightarrow}O{\leftarrow}N(=O)(=O)$ (8)

$\measuredangle(CON) = 110°$
$\mu(\text{observed}) = 2.9.$ $\quad$ $\mu = 0.3+0.9-1.4+4.0 = 2.9.$

Nitrous Oxide:

$N{\equiv}N{=}O$ $\quad$ $N^{III}{\leftarrow}N^{V}{\rightarrow}O$ (9)

$\mu(\text{observed}) = 0.2.$ $\quad$ $\mu = -4.2+4.4 = 0.2.$

Azide Group:

$—N{=}N{\equiv}N$ $\quad$ $—N^{III}{\leftarrow}N^{V}{\rightarrow}N^{III}$ (10)

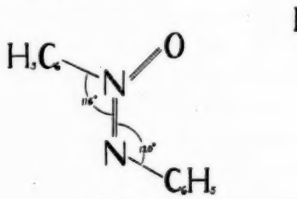
$\mu(\text{observed}) = 1.4$ to 1.6. $\quad$ $\mu = -2.8+4.2 = 1.4.$

Diazo Group:

$>C{=}N{\equiv}N$ $\quad$ $>C{\leftarrow}N^{V}{\rightarrow}N^{III}$ (11)

$\mu(\text{observed}) = 1.4.$ $\quad$ $\mu = -2.6+4.2 = 1.6.$

Azoxybenzene:



(12a) $\quad$ (12b)

$\mu(\text{observed}) = 1.7.$ $\quad$ $\mu(\text{calculated}) = 1.9.$

Iso-Azoxybenzene (with same angles and bond moments):

$$H_5C_6—N{=}O \\ \quad\quad\quad\quad \| \\ H_5C_6—N \qquad (13)$$

$\mu(\text{observed}) = 4.7,$
$\mu(\text{calculated}) = 4.2.$

p,p'-Azoxytoluene [with $H_3{\rightarrow}C{\rightarrow}(C_6H_4){\rightarrow}N^{III} = 0.3+0.6+0.9 = 1.8$, and $H_3{\rightarrow}C{\rightarrow}(C_6H_4){\leftarrow}N^{V} = -0.3-0.6+1.0 = 0.1$, otherwise same values]:

Normal: $CH_3—(C_6H_4)—N{=}O$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \| \qquad (14)$

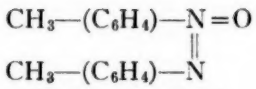
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad N—(C_6H_4)—CH_3$

$\mu(\text{observed}) = 1.7$ to 1.9,
$\mu(\text{calculated}) = 1.6.$

* In NOCl this angle has been observed to be 116° and such a value would change the following calculated moments by about 0.1D.

[14] L. E. Sutton, Trans. Faraday Soc. **30**, 789 (1934).

Iso:



(15)

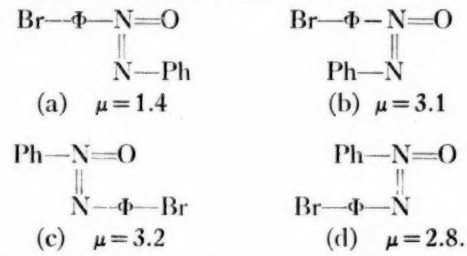
μ(observed) = 5.1,
μ(calculated) = 5.0.

o,o'-Azoxytoluene (calculated for free rotation of the tolyl radical):

Normal: μ(observed) = 1.9, μ(calculated) = 2.1. (16)

Iso: μ(observed) = 4.4, μ(calculated) = 4.1. (17)

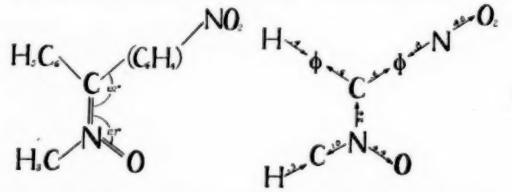
Mono-p-bromo Azoxybenzene: For the four possible structures the following moments are calculated (μ(Br←C_{AR}) = 1.1):



(a) μ = 1.4 (b) μ = 3.1 (c) μ = 3.2 (d) μ = 2.8. (18)

For two of them the moments have been observed as 0.9 and 2.6D, and these probably will have been structure (a) and (d). The induction of the halogen upon the ring is again apparent.

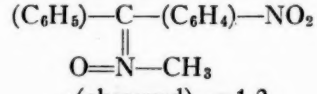
p-Nitrobenzophenone α-Oxime N-Methyl ether:



(19)

μ(observed) = 6.6. μ(calculated) = 6.4.

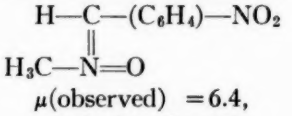
p-Nitrobenzophenone β-Oxime N-Methyl ether (with same angles and bond moments):



(20)

μ(observed) = 1.2,
μ(calculated) = 1.4.

p-Nitrobenzaldoxime N-Methyl ether (α):



(21)

μ(observed) = 6.4,
μ(calculated) = 6.2.

The agreement is very good, particularly as the bond moments used cannot be more (and do not claim to be more) than the very first rough evaluations and as individual changes of valence angles are bound to occur in such molecules. The result is the more remarkable, as among the more complex molecules are those whose electric moments have remained unexplained up till now. For the classical structures and their bond moments, however, no difficulty exists at all and they fall into line automatically. The dipole moments of molecules formed by pentavalent nitrogen would appear to make any other theoretical concept untenable. This paper set out (Part I and Part II) to show that physicochemical measurements such as these by their very nature are unable to distinguish between different types of covalent linkage. It would appear as if we have defeated our own ends; for these molecules, the dipole moments would seem definitely to decide in favor of the classical structures and against formulae containing a coordinate bond. Therefore, it may as well be admitted that with a sufficient number of resonance forms a description of any moment may be obtained. This is particularly so, as the percentage contribution of the parent structures is a variable factor. Such an adjustable element in a theory naturally makes it possible to represent any measured quantity, but by the same token it makes it impossible to prove the theory as such. For a theory which, by assuming different percentages of contributions of different forms, automatically can represent any experimental result, a crucial experimental test does not exist. The classical structures do not possess this advantage, but, on the other hand, representations such as this of the observed moments, for this very reason establish their validity and their inner congruence. Such an extremely simple and straightforward description of the electric properties of the molecules by means of definite additive bond moments for each valence state is, therefore, superior at least by virtue of the principle of economy of hypotheses.

BOND MOMENTS AND ATOMIC NUMBER

The bond moments derived so far, together with some calculated by Smyth[2] for the lower valence states, are collected in Table I. Mostly they represent values taken from one particular

TABLE I. Bond moments.

N^{III}—C	−0.5						
N^{III}=C	−0.9						
N^{III}=O	2.0						
		P^{III}—Cl	0.8				
N^{V}—C	(1.0)	P^{V}—C	(∼1.3)				
N^{V}=C	2.6						
N^{V}=N^{III}	2.8						
N^{V}≡N^{III}	4.2						
N^{V}—O	1.4						
N^{V}=O	4.4	P^{V}=O	6.2				
		P^{V}=S	5.4				
		P^{V}—Cl	3.7				
		S^{II}—C	−0.7				
		S^{II}—Cl	0.6				
		S^{IV}—C_{AR}	−2.2	Se^{IV}—C_{AR}	(∼3.8)	Te^{IV}—C_{AR}	(∼3.9)
		S^{IV}—O	0.6				
O^{IV}=O	0.6	S^{IV}=O	1.6	Se^{IV}=O	2.1		
		S^{IV}=S^{II}	1.5	Se^{IV}=Se^{II}	2.0		
		S^{IV}—Cl	1.1	Se^{IV}—Cl	1.4	Te^{IV}—Cl	2.6
		S^{VI}—C	0.4				
		S^{VI}—N	0.6				
		S^{VI}=O	3.9				
		S^{VI}—Cl	2.4				

molecule and measurement, and are still unnecessarily afflicted by fortuitous errors. They could be improved by taking the average of several observations of a number of similar molecules. However, this method of direct comparison without taking means appeared better suited for the present purpose, namely, to demonstrate the existence of constant and additive bond moments according to the state of valency. It will be seen that they are governed by three rules: (1) In an homologous series such as S^{IV}—Cl, Se^{IV}—Cl, Te^{IV}—Cl, the moment increases in this order. (2) In a series S^{IV}=O, S^{IV}=S, in which the negative atom varies, the bond moment decreases in the same direction. (3) A change of valency increases the moment, as shown by such examples as $\mu(P^{III}—Cl)=0.8$ and $\mu(P^{V}—Cl)=3.7$, $\mu(N^{III}=O)=2.0$ and $\mu(N^{V}=O)=4.4$, or $\mu(N^{III}—C)=-0.5$ and $\mu(N^{V}—C)=1.0$, reversing the direction. An exception to these rules appears to be offered only by the moment $\mu(S^{IV}—C)=-2.2$.

The absolute values even in the highest valence states are not very high. According to the basic concept as discussed in Part II, the values per electron pair have to be compared. For the nitro group this value is 2.2, not much higher than for HCl or H_2O, particularly if the bond distance is taken into account.

The electric moment measures the dissymmetry of the nuclear fields, and Mulliken[15] has suggested that this dissymmetry may be expressed in terms of the ionization potential (I) and the electron affinity (E). Accordingly in a bond $A-B$ the quantities $[I(A)+E(A)]/2$ and $[I(B)+E(B)]/2$ describe the dissymmetry of the fields, and their ratio, therefore, the polarity of the bond. In the preliminary discussion of Part II of this series,[1] this concept has been used, and indeed these three empirical rules could be stated as follows: (1) In comparing, e.g., S^{IV}—Cl and Se^{IV}—Cl, the ionization potential of Se^{IV} is smaller than that of S^{IV}, the electron affinity and ionization potential of Cl remain unchanged, hence, the moment increases from S to Se. (2) Conversely, the electron affinity and ionization potentials of O^{II} are larger than those of S^{II}, hence, S^{IV}=O exhibits a larger moment than S^{IV}=S. (3) In the transition to a

[15] R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934); **3**, 573, 586 (1935).

higher state of valency the mean ionization potential of the central atom increases as two electrons are transferred from atomic to molecular orbitals and the field of the core becomes vastly more positive.

A more detailed discussion, however, reveals at once that this concept is only approximately valid. Its physical meaning is that the binding electrons are shifted in the direction of the nucleus with the stronger electric field. Already in molecules like PCl_3 it is in reality the P atom which is surrounded by the stronger field, but the moment points in the direction of the Cl atom and special further assumptions have to be introduced. In the cases under discussion here, the higher the valence state, the higher the nuclear field of the central atom. But empirically the moment always points away from it, with the one exception of the S^{IV}—C moment. The reason for this discrepancy is that ionization potential and electron affinity measure the strength of the nuclear fields only when the atoms are at infinite separation, but not in the completed molecule at small internuclear distance, or rather they do so only in the first approximation.

If the wave function of the molecule AB be written according to the method of molecular orbitals, namely, as

$$\psi_{AB}=\{a\psi_A(1)+b\psi_B(1)\}\{a\psi_A(2)+b\psi_B(2)\},$$

the dissymmetry of the fields is expressed by the ratio of the coefficient a^2 and b^2. But these can be expressed as simple functions of ionization potential and electron affinity only, as long as nonlocalized molecular orbitals are used (Mulliken) or the interaction of the electrons is omitted (Hund). In both procedures as pointed out before,[1] the resonance effect of Heitler and London is neglected, and we obtain a description of the electron configuration and term system of the molecule, but no valid statements can be made as to its energies. Hence, all questions as to valency and the formation of the molecule remain unanswered, among them that of the polarity of the bond. If written according to the requirements of the electron-pair bond theory as:

$$\begin{aligned}\psi_{AB}&=ab\{\psi_A(1)\psi_B(2)+\psi_B(1)\psi_A(2)\}\\&\quad+a^2\{\psi_A(1)\psi_A(2)\}+b^2\{\psi_B(1)\psi_B(2)\}\\&=ab\psi(A-B)+a^2\psi(B^+A^-)+b^2\psi(A^+B^-),\end{aligned}$$

the ratio of the normalizing factors a^2 and b^2 again measures the polarity of the bond. But here, both a and b themselves depend on the internuclear distance. They are simple functions of ionization potential and electron affinity only for separated atoms at infinite distance; otherwise, indeed the bond moment always would be directed against that atom whose core has the stronger field in the isolated state. Then, of course, the interaction of the atoms vanishes and the same result obtains as before, namely, that a^2 and b^2 are proportional to the sum of ionization potential and electron affinity only, when the electron resonance is not present.

However, as the second function also represents Pauling's resonance concept, we may measure the ratio of a^2 and b^2 by means of the energy differences between the energy level which constitutes the molecule $A-B$ and those of the forms (B^+A^-) and (A^+B^-). For reasons discussed earlier, which are even more valid for these higher valence states, we do not attempt to formulate absolute values. Nevertheless, one relation is obvious. The energy difference between $(A-B)$ and (A^+B^-) is an energy of "excitation" between two terms of the same molecule, and applying the well-known band spectroscopical equation which expresses the energy of the (O, O) band of a band system in terms of the atomic excitation and the dissociation energies (D) of lower and higher state, we may write for the energy difference of the completed molecules at small internuclear distance $\Delta=I(A)-E(B)+D(A-B)-D(A^+B^-)$. If the ground level of the molecule is $(A-B)$, then the lower the excited term with the electron configuration (A^+B^-) (i.e., the more the electrons shifted towards B), the larger will be the coefficient b^2. Hence, Δ should be proportional to $1/b^2$. A similar simplified relation obtains for a^2, and the dissymmetry of the fields will be characterized by:

$$\frac{b^2}{a^2}\sim\frac{I(B)-E(A)+D(A-B)-D(A^-B^+)}{I(A)-E(B)+D(A-B)-D(A^+B^-)}.$$

In such a formula, the dissociation energies include the missing terms of the electron resonance.

Often the dissociation energies $D(A-B)$, $D(A^+B^-)$, and $D(A^-B^+)$, although different, still will be of the same order, and will compensate or

nearly so. This is the case in simple molecules like HCl. The two ionic terms will nearly counterbalance each other also in simple molecules with double bonds, like CO or SO. In each case the polarity may still be considered as proportional to the ratio of ionization energy plus electron affinity of both atoms.

However, when proceeding to higher valencies, e.g., from SO to SO_2, conditions change. In a bond such as $S^{IV}{=}O$, four valence electrons are in the fields of S^{4+} and O^{2+}. The term (A^+B^-), therefore, contains, among others, contributions of forms in which all four electrons are with O, i.e., of $(S^{4+}O^{2-})$. The corresponding term of (A^-B^+) contains forms in which all four electrons are with S, but this gives us $(S\,O^{2+})$. The dissociation energy of such a molecule comprising a neutral atom and an ion, is of the order of the van der Waals or association bonds, while $D(S^{4+}O^{2-})$ is overwhelmingly larger. Their difference easily can be greater than that of $(I(S^{4+}) - E(O^{2-}) - I(O^{2+})$. As a matter of fact, if $D(S^{4+}O^{2-})$ is taken as twice that of $(Ca^{2+}O^{2-})$, which has a similar internuclear distance, the level $(S^{4+}O^{2-})$ will be several electron volts below that of $(S\,O^{2+})$, although for the separated systems $(S^{4+}+O^{2-})$ and $(S+O^{2+})$ the former is much higher than the latter on account of the high ionization energy of S^{4+}. Hence, in such a case, b^2 is larger than a^2 in spite of $I(B)$ being smaller than $I(A)$, and the moment points away from the central atom. If, however, oxygen is replaced by CH_3 with its low ionization potential of 11 ev, the energy difference between the separated systems becomes so large that an intersection of the terms on decreasing internuclear distance cannot come to pass, and a^2 remains larger than b^2, i.e., the moment points towards the central atom as in the sulphoxides.

These conditions may be expressed slightly differently in the language of the resonance concept. If $A-B$ is a simple molecule like HCl or SO, then the forms (A^+B^-), e.g., (H^+Cl^-), or (S^+O^-) and $(S^{2+}O^{2-})$, and the forms (A^-B^+), e.g., H^-Cl^+ or (S^-O^+) and $(S^{2-}O^{2+})$, may already be markedly different in their energetic contributions, but are still of the same order. For higher valence states, in which the positive atom A carries a much higher positive charge than the negative atom B, this is not so, and the contributions of (A^+B^-), among them such as $(S^{4+}O^{2-})$, are not in the least compensated by those of the forms (A^-B^+). Hence, the forms (A^+B^-) play the much greater role and direct the bond moment against B, although the stronger field goes with A. It is this feature which may be expressed[1] as the addition of a positive charge to the plus end of the dipole at the transition of the central atom to a higher valence state, without corresponding shift of the electrons.

CONCLUSION

For simple molecules formed by a central atom in a higher state of valency, a number of bond moments have been calculated on the basis of the classical formulae. These are then applied to other more complicated molecules. For each combination of two atoms a definite bond moment obtains, which remains unchanged for this combination as long as the state of valency and the multiplicity of the bond remain the same. The bond moments are additive in the same molecule and are constant from one molecule to the other. As a matter of fact, they remain more constant than might have been expected under the varying effects of induction, solvation, and slight changes of the valence angles. This indicates all such bonds to be of the type of ordinary covalency, the valence electrons firmly localized between two atoms.

The dipole moments of a considerable number of these molecules have not been rationally explained before. It would be possible, therefore, to conclude that these classical structures are a better approach to reality than any other concept. In any case, they describe the electric properties of the molecules at least as well as any other theory. Hence, it is obvious that dipole moments do not possess any diagnostic quality, which permits them to distinguish between semipolar or normal covalency, or between two different theories of the covalent linkage. For molecules of Werner's first order, formed by a marked central atom, dipole moments, therefore, do not provide evidence for the existence of semipolar bonds or of enhanced resonance with ionic parent structures.

Letter to the Editor

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The Surface Area of Crystalline Egg Albumen

T. M. SHAW
Western Regional Research Laboratory, Albany, California
June 27, 1944

THE method of Brunauer, Emmett, and Teller (BET)[1] has been used extensively for the determination of the specific surface areas of adsorbents. In most instances so far reported the areas obtained for a given adsorbent are independent of the adsorbate.[2-4] However, a significant difference has been noted for the clay mineral montmorillonite.[5,6] In this instance the surface area evaluated from the water vapor adsorption isotherm exceeds the surface area found from the nitrogen adsorption isotherm by about 50-fold. Recent adsorption measurements on crystalline egg albumen in this laboratory have revealed even larger differences in the surface areas available to water vapor and to nitrogen. Samples of native egg albumen were prepared by dialyzing solutions of previously crystallized egg albumen against distilled water followed by vacuum-drying from the frozen state. The drying was continued at room temperature (about 25°C) until the total pressure in the system was less than 5×10^{-6} mm Hg.

The adsorption of nitrogen at −183° and water vapor at 25° was measured in an apparatus similar to that described by Emmett.[3] In Fig. 1 are presented the adsorption data plotted according to the BET method. Assuming the average areas occupied by N_2 and by water molecules to be 15.4 and 10.6A², respectively,[7] the data in Fig. 1 yield surface areas of 2.42 sq. meters (for nitrogen) and 210 sq. meters (for water) per gram of egg albumen. The difference between the heat of adsorption in the first adsorbed layer E_1 and the heat of liquefaction E_L is 648 cal./mole for N_2 and 1100 cal./mole for water as calculated from the BET plots of Fig. 1. The water vapor adsorption data of Barker[8] for native egg albumen yield a surface area of 220 sq. m/g and E_1-E_L equal to 1280 cal./mole.

If one attempts to interpret these surface areas in terms of an average particle size it is found that the average particle diameter calculated from the surface available to nitrogen is 2×10^{-4} cm. A crystallite of this size would contain about 10^8 egg albumen molecules. Similarly the surface available to water would indicate an average particle diameter of about 2×10^{-6} cm, containing about 100 egg albumen molecules.

In the case of montmorillonite, however, it has been conclusively shown[4] that the discrepancy between the areas calculated from N_2 and water adsorption is due to the penetration of water in the polar region between the silicate layers. These polar layers are not penetrated by N_2 and the latter is presumed to cover only the external surface of the crystallites.

It appears of interest to consider the possibility that a similar behavior can account for the surface areas obtained for egg albumen. It has recently been proposed[9] that the native egg albumen molecule is composed of polar layers, giving rise to two intermolecular and one intramolecular polar interfaces, each approximately 1600A² in area. This model agrees with the experimental value of the surface

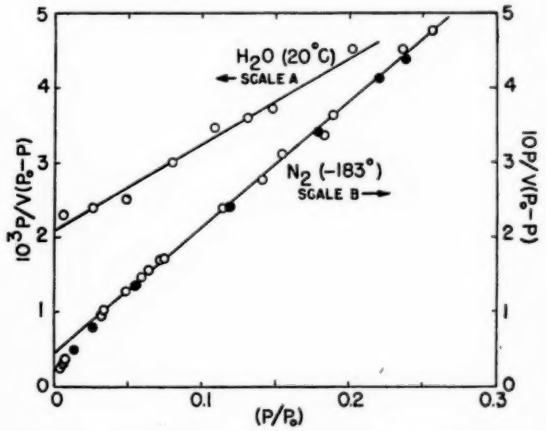

FIG. 1. Adsorption of nitrogen and of water vapor by 1 gram of egg albumin plotted according to the Brunauer, Emmett, and Teller theory. Filled circles are desorption values. V is volume in cc at S.T.P. adsorbed at pressure P. P_0 is the liquefaction pressure.

area available to water vapor if it is assumed that water is adsorbed only in the intermolecular polar interfaces. The area then available to water would equal 225 sq. m/g in good agreement with the experimental value of 210–220 sq. m/g. This suggestion is compatible with the fact that Astbury and Lomax[10] have obtained x-ray diffraction photographs for egg albumen showing that only the side chain spacing is affected by water vapor adsorption.

If one were to assume that water vapor is uniformly adsorbed on all external surfaces of the egg albumen molecule the surface available would be either about 675 or 1350 sq. m/g, depending on whether each monolayer of water is assumed to be shared or not. In any case this area would be from 3- to 7-fold larger than the experimental value.

The data presented above serve to emphasize that methods of determining surface areas from adsorption data must be used with due regard for the surface available to the particular adsorbate used. In studies where the area desired is that of the organized crystallites it must be first determined that the adsorbate is not able to penetrate the molecular lattice. Gases such as nitrogen and argon appear to satisfy this requirement in all particulars.

Grateful acknowledgment is made to Dr. K. J. Palmer for his interest and suggestions relative to the above work.

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